THE MANUFACTURE OF SULPHURIC ACID AND ALKALI

SUPPLEMENT TO VOLUME I.

SULPHURIC AND NITRIC ACID

WITH THE

COLLATERAL BRANCHES

A THEORETICAL AND PRACTICAL TREATISE

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SULPHURIC AND NITRIC ACID

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PREFACE

THE fourth edition of my treatise on the Manufacture of Sulphuric and Nitric Acid, etc., was published in February 1913, and has met with general approval on the part of the numerous class of persons interested in that important domain of technical chemistry. Since the issue of the fourth edition very numerous contributions have been made to the industries described therein, by patent specifications and by publications in the professional literature of all industrial countries. I have also obtained various communications from private sources on the subjects treated in this book. Very naturally most of its readers are desirous of becoming acquainted with this new matter, and the publishers have informed me of the great number of inquiries addressed to them thereon. The general wish seems to be for a Supplement giving an account of the new matter, without compelling the purchasers of the last edition to buy an entirely new edition, and the present volume is intended to meet that desire.

In order to facilitate the use of this Supplement in connection with the edition of 1913, it has been provided with alphabetical indices, comprising both the matter contained in the last edition and that added in the Supplement, distinguishing the latter by putting them in brackets: ( ).

I trust that this volume will meet with the same favourable reception as the main work

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SULPHURIC ACID AND ALKALI

SUPPLEMENTARY VOLUME

CHAPTER II

THE RAW MATERIALS OF THE SULPHURIC-ACID MANUFACTURE, INCLUDING NITRIC ACID

SULPHUR.

Page 13. *The atomic weight of sulphur* has been found by T. W. Richards and C. R. Hoover (*J. Amer. Chem. Soc.*, 1915, xxxvii. p. 108) = 32·065.

Page 14. *The boiling-point* of sulphur has been found by Eumorphopulos (*Roy. Soc. Proc.*, London, xcvi. p. 189) = 444·61°; by Chappuis (1914) = 444·55°.

Phosphorescence of sulphur. Researches on this point have been made by Heumann, Baker, Moissan, Bloch (*Comptes rend.*, 1909, pp. 148 and 782; *Ann. Chim. Phys.*, 1911, xxii. p. 460); Watson (*Chem. News*, cviii. p. 187).

Aten (*Z. physik. Chem.*, 1913, lxxxiii. p. 443) describes a *new modification of sulphur*, produced by heating it to 170°, to the extent of 5 per cent. It is soluble in sulphur chloride, toluene, and carbon disulphide. Its solutions possess a strongly yellow colour (the solutions of ordinary sulphur being colourless).

T. Hoffmann (*Z. f. Chem. and Ind. der Kolloide*, 1912, p. 275), who has obtained blue-coloured substances by fusing sulphur with potassium or with phosphorus pentachloride at a red heat.

Page 15. Researches on the *modifications of sulphur*, besides those mentioned in the text, have been made by Aten (*Z. physik. Chem.*, 1912, p. 257; 1913, p. 442); Leeuw (*J. Chem. Soc. Abstr.*, 1913, ii. 40); Beckmann (*Chem. Zentr.*, 1913, ii. p. 337); Gaubert (*Comptes rend.*, 1916, p. 554; *J. Soc. Chem. Ind.*, 1916, p. 600).

About *colloidal sulphur*, refer to our text, p. 50.

Sulphur containing selenium (5·18 per cent.) is described by G. V. Brown in *Amer. J. Sci.*, 1916, xlii. p. 132 (*J. Soc. Chem. Ind.*, 1916, p. 926).

Page 15. *The free energy of the various modifications of sulphur* has been investigated by Lewis and Randall (*J. Amer. Chem. Soc.*, 1914, xxxvi. p. 2259).

Page 15. *Solubility* of sulphur. The Chemische Fabrik von Heyden Akt. Ges. (Ger. P. 284410) dissolves sulphur (as well as paraffin and ozokerite) in liquid tricresylphosphate, prepared from crude cresol and chlorinated cresol. This agent dissolves the sulphur out of vulcanised india-rubber, leaving the india-rubber behind in the shape of an elastic mass.

Further researches on the behaviour of sulphur against water and aqueous solutions of acids and salts have been made by Smits (*Z. physik. Chem.*, lxxxiii. p. 221); de Leeuw (*ibid.*, p. 245).

Coloured solutions of sulphur in various solvents are described by Weimarn (*J. Russ. Phys. Chem. Soc.*, 1915, xlv. 2177; extr. in *J. Chem. Soc. Abstr.*, 1915, ii. p. 185).

the text, p. 16. According to a second paper by the same author (*Comptes rend.*, clvi. pp. 725 *et seq.*), this fertilising action of sulphur is sometimes very strong, especially when applied on potato cultures. He ascribes it partly to its action on the micro-organisms of the soil, and partly to its gradual conversion into sulphuric acid, which causes the solution of some elements of the soil. The action of sulphur is, however, lessened or even annihilated by the presence of large quantities of organic or mineral manures.

Several papers on this subject have been published by Heinze (*Chem. Zentr.*, 1906, ii. p. 699; 1907, ii. p. 270; 1913, i. p. 2173).

Thalau (*Vers. Stat.*, 1913, p. 161; *Z. angew. Chem.*, 1913, ii. p. 601) states that the action of sulphur as a fertiliser is not to be explained in a simple manner, and he does not believe in such an action on our culture plants.

Bosinelli (*J. Soc. Chem. Ind.*, 1915, p. 1064) states that the action of a dressing of free sulphur produces no effect on the crop. It accelerates the conversion of organic nitrogen into ammonia compounds, but the effect is very small.

Molz (*Z. angew. Chem.*, 1913, i. p. 534) does not believe that the fungicide action of flowers of sulphur is caused by the SO_2 contained therein, since oïdium spores can be brought to germinate in a dilute solution of sulphurous acid. The oïdium is much more affected by the H_2S, formed from the sulphur, and probably also in a physical way. He states that the fungicide action of sulphur is frequently employed in fruit and garden cultures, especially for combating the various descriptions of mildew, and the damaging action of mites, earth-fleas, and earwigs.

Rupprecht (Ger. P. 290240) points out that when employing

p. 845) found next to no acid in roll sulphur, but in 100 g. flowers of sulphur up to 3·14 c.c. SO_2, partly converted into H_2SO_4.

According to Vogel (*Chem. Zentr.*, 1914, i. p. 1212), the action of sulphur, when mixed with soil, is favourable to the cultures. The best proportion is from 15 to 20 mg. on 500 g of the soil. But according to Pfeiffer and Blanck (*Z. angew Chem.*, 1914, ii. p. 298), sulphur, applied on an experimental field, caused neither an increase of the production of vegetables nor a better utilisation of the nitrogen contents of the soil, but *vice versa* a slight diminution in both directions. They do not however, doubt that sulphur may be useful in certain cases especially for combating fungoid diseases (*J. Soc. Chem. Ind.* 1915, pp. 294 and 1106).

H. Clay Lint (*J. Ind. Eng. Chem.*, 1914, p. 747) found tha sulphur, applied to the soil, is oxidised within eight or nin weeks, with corresponding increase of the sulphates.

Thörner (*Z. angew. Chem.*, 1916, i. p. 233) describes th action of free sulphur, contained in marshy soil, on th vegetation.

Page 16. *The formation of free sulphur from sulphates b the action of bacteria* has been studied by Doss (*Chem. Zentr* 1913, ii. p. 1252).

The formation of sulphuric acid from free sulphur has bee studied by Zänker and Färber (*Chem. Zentr.*, 1913, ii. p. 907 1914, ii. p. 1219). Sulphur, deposited on cotton, forms sma quantities of free sulphuric acid, either by itself or by th co-operation of the porosity of the fibre. Free sulphuric aci is also present in the various descriptions of commercial sulphu but is found only by very exact methods, most of it in flowe of sulphur, much less in roll sulphur. Colloidal sulphur, aft being washed,

United States and Canada	8,560	7,125	1,792	2,154
France	105,300	112,897	79,327	96,156
Italy (mainland)	75,400	78,954	82,348	108,916
Germany	28,660	28,869	35,091	391
Norway, Sweden, Denmark	30,200	29,913	38,092	24,781
Greece and Turkey	25,300	15,596	19,792	19,857
Great Britain	19,800	20,764	17,540	36,156
Russia	23,485	22,838	27,358	2,791
Austria and Hungary	35,700	37,265	34,543	1,163
Holland	12,650	12,625	12,518	12,784
Portugal	22,550*	14,185	14,758	...
Belgium	10,300	12,152	12,399	8,220
Spain	...	6,952	7,036	...
Other Countries	58,325	47,503	51,479	47,635
Total	...	447,638	434,473	359,806

* With Spain.

The *total production of sulphur* in Italy in 1911 was 456,200 tons; in 1912, 389,451 tons crude sulphur, and 333,378 tons purified sulphur, of which 164,884 tons was ground (*Chem. Zeit.*, 1914, p. 866); in 1913, 346,213 tons; in 1914, 381,978 tons.

The production of the Sicilian works from 1st August 1913 till 31st July 1914 was 340,925 tons, the quantity sold 404,712 tons, at an average price of 94·76 lire per ton (*Chem. Ind.*, 1915, p. 77).

According to *U.S. Cons. Reps.*, 18th August 1915, the production of sulphur in Sicily in the year 1914 was 334,974 metric tons, the exports 338,308 tons.

Page 22. *Statistics of Sulphur for other Countries.*—Great Britain in 1912 imported 435,201 cwt.; in 1913, 364,285 cwt.

Germany in 1911 imported 46,054 tons; in 1912, 42,284 tons; in 1913, 46,737 tons.

Austria-Hungary in 1912 imported 40,800 tons, and exported in the liquid form (*J. Soc. Chem. Ind.*, 1915, p. 399). In the year ending 31st August 1914 the exportation from Japan was 23,310,156 lb.; in that ending 31st August 1915, 27,948,607 lb.

In New Zealand (according to the Government Commissioner's Report, *Chem. Trade J.*, li. p. 300) in 1912 a limited company, with a capital of £100,000, bought White Island in the Plenty Bay, with the object of working the sulphur deposits existing on an area of 40 acres, with 84 per cent. pure sulphur, and hot springs emitting streams of sulphur (94 per cent. S). In 1914 (according to *Chem. Zeit.*, 1915, p. 244), at present 1000 tons per month is obtained, but this production is to be increased to 30,000 tons.

In Central Asia, at Karakum, about 150 miles north of Ashabad, there is an extensive deposit of sand containing from 60 to 90 per cent. sulphur, which cannot be utilised at present owing to the great distance. At At-Chagyl, alongside of the salt lake of Kukurt-Ata, 62 versts from Krosnovodsk (Russia), the exploitation of an immense sulphur deposit, with 90 per cent. pure sulphur, was begun in 1916.

Page 26. *Occurrence of Sulphur in Louisiana.*—This is further described in *Mineral Resources of the United States*, 1911, p. 940; and by Pough in *J. Ind. Eng. Chem.*, 1912, pp. 143 *et seq.*

The Union Sulphur Company sells the Louisiana sulphur guaranteed to contain 99, 5 per cent. S, and to be free from arsenic and selenium.

Sulphur in Texas.—The sulphur bed in the valley of the Brazos River is worked since 1913 by the *Freeport Sulphur Co.*, with a capital of 1½ million dollars. According to Vail (*Eng. and Min. J.*, 1912, p. 449), that company works by a process similar to that of Frasch (our text, pp. 30 *et seq.*); it is intended to produce 120,000 tons sulphur per annum, at such

		Crude Sulphur (mostly from Sicily).	Flowers of Sulphur.	Refined Sulphur.	imported.
	Tons.	Tons.	Tons.	Tons.	Tons.
1912	303,412	26,885	1,311	1,665	29 927
1913	311,590	15,122	5,899	1,234	22,605
1914	327,634	23,610	621	1,800	26,135
1915	...	24,647	647	988	25,910

The exportation of sulphur from the United States has been, in 1907, 35,925 tons; in 1908, 27,894 tons; in 1909, 37,142 tons; in 1910, 30,742 tons; in 1911, 28,103; in 1912, 57,736 tons; in 1913, 89,221 tons; in 1914, 98,153 tons; in 1915, 37,312 tons.

Page 28. *Sulphur deposits in Chili.*—According to *Chem. Ind.*, 1913, p. 403, in the year 1911, 4451 tons sulphur was produced in the Aricas District, in the province of Tacua. The importation of sulphur into Chili was in that year 4014 tons.

According to *Chem. Zeit.*, 1915, p. 799, the production of sulphur in Chili in 1913 was 6647 tons.

In *Argentina* a sulphur bed has been discovered at a height of 6500 feet (*Chem. Zeit.*, 1915, p. 788).

Page 29. *Production of Sulphur in the whole World*—In *Z. angew. Chem.*, 1915, iii. p. 366, this is stated as follows in tons of 1000 kil.:—

	1912.	1913.	1914.
Italy:—			
Sicily	356,531	345,349	334,978
+ Internal use . .	10,000	10,000	10,000
Elsewhere . .	37,497	38,722	37,000
	404 028	391,071	381,978
United States . . .	308,328	316,575	381,018

by this process. There were employed for it 130 steam boilers of from 180 to 300 horse-power each, fired by petroleum, of which over a million barrels were used. The daily consumption of water was about 7 million gallons; the daily production of a well, sometimes 400 or 500 tons sulphur; the annual production more than 250,000 tons.

A new patent for mining sulphur by the fusion process from a water-flooded porous deposit was taken out by H. Frasch as U.S. P. 1152499, and assigned to the Union Sulphur Company.

Page 35. The Austrian patent granted to Sanfilippo di Luigi for the production of sulphur from its ores is No. 55235.

Page 35. Huff (Assignor to Moss), U.S. P. 1184649, employs a well-casing, closed at the top, with perforations near the bottom, near to which electrical heaters are mounted. Water supplied to the casing is heated therein, and passes through the perforations into the sulphur-bearing strata. The molten sulphur is raised to the surface through an inner pipe, which passes down and projects beyond the bottom of the casing.

Page 37. Urbasch (Ger. P. 294912) distils the sulphur off by means of producer-gas.

Page 38. *Production of Sulphur from Spent Oxide of Gas-works.*—Hunt and Gidden (B. P. 8097 of 1912; U.S. P. 1059996; Chance and Hunt, Fr. P. 452034, and Ger. P. 263389) heat the mass above the fusing-point of sulphur, extract the oxides, etc., by sulphuric acid of spec. grav. 1·60, and extract the sulphur from the residue by means of a solvent. Or the spent oxide is first treated with a solvent for sulphur, and the tar-containing sulphur treated as above.

The Société d'Eclairage, Chauffage et Force motrice (Fr. P. 454990) extract the sulphur by means of light tar-oils (boiling between 150° and 190°) at 100°, which dissolved 35 to 40 per cent. sulphur. The sulphur remaining behind is described in detail in our Vol. II., 3rd edition (1909), pp. 943 *et seq.*

Page 38. *Sulphur from Coal-gas.*—Ciselet and Deguide (Ger. P. 288767) obtain sulphur and cyanogen compounds from the gases produced in the distillation of coal, by treating them with precipitated ferric hydrate. After using this over and over again, until the mass is sufficiently enriched in sulphur and cyanogen, the ferric hydrate is dissolved by sulphuric or hydrochloric acid, and from the residue sulphur and ferrocyanide are obtained in the well-known way.

Page 40. *Sulphur from Pyrites.*—The U.S. P. of Stickney is No. 475824.

W. A. Hall (B. P. 20759 of 1912; U.S. P. 1083248; Fr. Ps. 455005 and 458028) submits the gases produced in a mechanical pyrites burner of his own construction in turns to the action of steam and to that of a reducing flame, whereby hydrogen sulphide and free sulphur are formed. His B. P. 20760 of 1912, *vide infrà*, p. 16, describes the conversion of the hydrogen sulphide into free sulphur. According to a report, quoted in *Z. angew. Chem.*, 1913, iii. p. 573, from "Mining Science," the First National Copper Company at Coram (Cal.) was going to introduce this process, heating sulphide ores in a neutral or reducing atmosphere, whereby the sulphur is volatilised in the free form and collected in water, or precipitated by means of Cottrell's electrical process, whilst the metal remains in the shape of oxide. According to the reports given in *Eng. Min. Journ.*, 5th July 1913, and *J. Ind. Eng. Chem.*, 1913, p. 955, all the sulphur, down to 1 per cent., remaining in the residue, can be removed and recovered by submitting the ore to a flame of non-oxidising or reducing character, together with water in vapour, no SO_2 or H_2S, escaped. The residues consisted of a mixture of Fe_2O_3 and Fe_3O_4. The temperature in the furnace should not be below 700° nor above 900°, which would cause the sulphides to fuse. The consumption of coal is theoretically $=0$; practically below 10 per cent. of the weight of the ore. The cost of the process in American smelting works is from 3 to 5 dols. per ton of the crude sulphur produced. The sulphur is precipitated from the gases by simply washing them with water. The crude sulphur produced contains from 98 to 99½ per cent. S; the impurities consist of ore dust or sulphides of lead or zinc. The purified sulphur contains over 99½ per cent. sulphur of the octahedric and prismatic variety, soluble in carbon disulphide. This process has been worked out in the first line for roasting-ovens with several hearths, but promises to succeed also with blast-furnaces.

Further patents of W. A. Hall (B. Ps. 26370, 26594, 26595, of 1912; 8279 of 1913; U.S. P. 1133626) contain further rules for carrying out the process. According to these the application of steam may be dispensed with. Part of the pyritic sulphur is distilled off by the direct action of a reducing flame; the residue is roasted, whereby the sulphur goes away as SO_2; the SO_2 is converted into H_2S, and this is burned in the reducing flame formed in the first distillation, whereby the S of the H_2S is obtained.

According to *Met. Chem. Engin.*, 1914, p. 718, the smooth working-up of the sulphur vapour formed in this way still causes difficulties. The Feld washer employed for this purpose was soon stopped up.

Further patents of W. A. Hall (U.S. Ps. 1083248, 1083249, 1083250, 1083251, 1083252, 1083253; Fr. P. 458028) refer to the application of his process to other metallic sulphides, such as zinc-blende, copper pyrites, galena, and give further details on his process.

Sufficient hydrogen sulphide is thus generated in the upper portion of the furnace to reduce the SO_2 in the furnace gases, and prevent combustion of the free sulphur produced. The flame of a reducing gas is introduced into the furnace, under conditions whereby SO_2 in the exit gases is reduced to sulphur.

Hall's processes are described in detail by Wierum in *U.S. Min. Res.* for 1914, p. 138.

According to Schiffner (*Chem. Zeit. Rep.*, 1914, p. 383), the Cottrell electrical process for separating dusty particles from gases, mentioned *suprà*, is working in a series of large American smelting works. According to the experiments made at Freiberg, it may be taken as proved that, when choosing the proper conditions, by this process liquid and solid particles floating in the gases may be precipitated.

Drakeley (*J. Chem. Soc.*, 1916, cix. p. 723) discusses the influence of pyrites on the oxidation of coal.

The British Sulphur Company, Ltd. (Austr. P. appl. A6907) obtain the total sulphur of ores in the free form by means of a reducing flame, containing an excess of hydrogen, and just enough oxygen to burn the hydrogen, and to convert any H_2S formed into H_2O and free sulphur.

The New Jersey Zinc Company, New York (U.S. Ps. 1103081 and 1103082), obtain sulphur by heating pyrites, with exclusion of air, to 600° to 800°, until it has passed over into pyrrhotite or magnetic sulphide. When treating blende in this way, the iron sulphide formed can be extracted by magnetic means.

Page 41. *Production of Sulphur from other Metallic Sulphides.*—Dekker (Ger. P. 245768) treats metallic sulphides (especially galena, zinc sulphide containing iron, pyrites containing gold, copper, nickel, etc.) by mixtures of sulphates and sulphuric acid, preferably 1 mol. $ZnSO_4$ or Na_2SO_4, 1 mol.

process, and reconducting it over the materials, together with further quantities of superheated steam.

Kingsley (U.S. P. 1144480) heats sulphides with dilute nitric acid (containing at most 5 per cent. HNO_3), whereby, together with metallic nitrates, free sulphur is obtained.

Page 41. *Production of Sulphur by passing Gases containing Sulphur Dioxide through red-hot Coal or Coke.*—The first mention of this process is made in a pamphlet of Vivian in 1833; Reich describes experiments made with it at Frankfort in 1858. The German patent for the process of Haenisch and Schroeder mentioned in the text is No. 33100.

Scheurer-Kestner (*Comptes rend.*, cxiv. p. 296) has examined the reactions going on; the principal of these is

$$2SO_2 + 3C = 2CO + CO_2 + 2S.$$

Bémelmans (Ger. P. 77335) reduces the SO_2 by carbon and hydrogen to H_2S, dries the latter, mixes it with dry SO_2, and causes the decomposition into H_2O and S.

Jungfleisch and Brunel (*Acad. d. sciences*, 28th July 1913) examined the formation of free sulphur by the action of SO_2 on water. First hydrosulphuric acid is formed, which decomposes into sulphuric acid and free sulphur. The state of the latter depends on the temperature of the reaction. Above 113° the sulphur is produced in the liquid state, and on cooling solidifies in the form of clinorhombic or of octahedric crystals, according to the temperature. Below 113°, *e.g.* at 100°, the sulphur is separated in the soft form; at 68° to 70° as globules of soft, isotropic sulphur, which pass over into crystals (globulite and crystallite).

Lamoureux and Renwick (B. P. 2834, 1915; U.S. Ps. 1140310 and 1182915; Fr. P. 477795) reduce SO_2 contained in gases, mixed with atmospheric oxygen, to elemental sulphur by *fumes*).—The "Thiogen process" of the Pennsylvania Manufacturing Co., described by S. W. Young (*J. Soc. Chem. Ind.*, 1913, p. 293), depends upon the reduction of sulphur dioxide by ethylenic hydrocarbons according to the reaction,

$$3SO_2 + C_2H_4 = 3S + 2CO_2 + 2H_2O,$$

which, however, is very slow and incomplete. This is avoided by employing a catalyser, viz., ferric oxide or calcium sulphide containing such, which brings about the cyclic reaction,

$$2CaS + 3SO_2 = 2CaSO_3 + 3S;$$
$$2CaSO_3 + C_2H_4 = 2CaS + 2CO_2 + 2H_2O.$$

The roaster gases containing about 8 per cent of SO_2 are passed first through a dust settler to a combustion chamber, where a certain amount of oil is introduced, and in which the excess of oxygen in the gases is burnt out. Thence the gases pass to the contact chamber, where more oil is introduced, the total amount being that which is necessary to burn out the oxygen and reduce the sulphur dioxide. The contact material is made up from plaster of Paris, which is mixed with water containing iron salts, allowed to set, and broken into lumps. The chief chemical difficulty is the contact mass being rendered inactive either by the presence of flue-dust, or by the destruction of its porosity by too high a temperature in the contact chamber. In a sereis of trials in one unit of a battery of eight six-hearth MacDougal roasters, the same charge of contact material was run for periods of from ten to twelve days without loss of activity, the exit gases containing practically no SO_2. The exit-gases from the contact chamber pass through a cooling and condensing apparatus, where the sulphur is deposited. The combustion chamber is filled with a network of bricks, heated to about 800° by the oil introduced in the form of dust by means of steam injectors. The contact been built at Campo Seco, California.

For this process Young, for the Thiogen Company, has obtained the U.S. Ps. 1094656 and 1094767, Fr. P. 450786, and the Ger. P. 271002. His processes are described in detail in the *U.S. Min. Res.* for 1914, p. 139.

The Metallurgical Institution of the Freiberg Mining Academy, as reported by Schiffner (*Chem. Zeit.*, 1914, p. 383), has in 1914 examined the process of Young, as well as those of Hall (pp. 9 *et seq.*, 16) and of Cottrell (p. 9). The former (the "Thiogen process") promises success only in such cases where for some reason no sulphuric acid is to be made from gases containing at least 8 per cent SO_2. It has been introduced in one factory. The Hall process has been carried out only in a small experimental factory at Brooklyn. The Cottrell process is working in several large American metallurgical establishments.

Basset (B. P. 20716, 1913; Fr. P. 472957) passes the gases, previously purified from dust, through a tower filled with red-hot coke, where a mixture of carbon dioxide, oxysulphide, and monosulphide is formed. This is oxidised to sulphur and carbon dioxide in another tower, heated by the first, into which through a special pipe an excess of carbon dioxide is introduced.

Vadner (Ger. P. 276568) removes from the gases the solid impurities, mixes them with reducing gases, and passes them first through red-hot coke, then into a space where the sulphur is condensed, and ultimately again through a purifier, for which purpose apparatus is described.

The Chemische Fabrik Griesheim-Elektron (B. P. 1550 of 1914) reduces sulphur dioxide or sulphites to sulphur by means of spongy zinc.

Ruthenburg (B. P. 29030, 1912) passes the gases first through an electrically heated coke column, then through a a tower in which calcium sulphide solution is squirted about. The mixed solution of calcium sulphide and sulphate, collecting at the bottom together with the precipitated sulphur, passes through a vessel where the solids are deposited, and then through a funnel into a furnace where the sulphur is distilled off and condensed; the residue remaining in the furnace is mixed with coal, and from this mixture calcium sulphide is regenerated.

Page 46. *Sulphur from Sulphites.*—The Farbenfabriken vorm. Friedr. Bayer & Co. (Ger. Ps. 263167, 264920, 265167; Fr. P. 459713) obtain sulphur and sulphates from solutions containing sulphites and thiosulphates, by adding (3 or 4 per cent. of the weight of the salts) polythionates, and heating in open vessels; *e.g.*, a liquid containing 100 parts sodium tetrathionate, 77 sodium bisulphite, and 140 sodium sulphate. This remains at first clear when being heated to boiling, but suddenly a strong separation of sulphur takes place, whereupon the decomposition is quickly completed, and the liquid now contains only sulphate. In order to avoid explosions, they prefer converting 2 mol. bisulphite and 1 mol. normal sulphite by heating under pressure into sulphate and sulphur, through the quantitatively occurring reaction:

$$2NaHSO_3 + Na_2SO_3 = 2Na_2SO_4 + S + H_2O.$$

Hansen (U.S. P. 1101740) obtains free sulphur and sodium sulphate by heating a mixed solution of bisulphate and sulphite, in the molecular proportion 2 : 1, under pressure to a temperature of 160° to 170° during four or five hours.

The same (U.S. P. 1102911) obtains sulphur, together with sodium sulphate, by heating a solution of sodium sulphate, bisulphite, and polythionate.

substances (ammonia or sulphur dioxide, or both together), and by a quantity of sulphur dioxide insufficient for a complete oxidation of the thiosulphate into polythionate, so that unchanged thiosulphate is always present. According to *Chem. Zeit.*, 1913, p. 1580, this "polythionate process" was then being carried out at a gas-works and a coking-works, each of them with a daily production of from 60,000 to 70,000 cb.m. of gas. Both gases (SO_2 and H_2S) are allowed to act simultaneously or in succession upon the solution of the thiosulphates of such metals whose sulphides are soluble in water. Upon 1 part by weight of H_2S at least 1 part of SO_2, or upwards, is employed. The polythionates, formed by the excess of SO_2, are reduced to thiosulphates by treating the liquid by basic or reducing compounds, or by gases or vapours containing H_2S or NH_3, or both of these. The solutions formed may be used for washing out NH_3, either by themselves or together with H_2S. In the case of gases containing beside H_2S also NH_3, the addition of SO_2 is regulated so that, apart from the SO_2 required for decomposing the H_2S, another 2 parts by weight of SO_2 or more is added for each part NH_3. The thiosulphate solution is diluted from time to time, when the reaction is going on more slowly.

Nordin (Swed. P. 35040) promotes the reaction between H_2S, SO_2, and water by adding an acid, cooling, and precipitating the sulphur by an electrolyte.

R. von Walther (Ger. P. 262468) treats waste liquids from the manufacture of sulphite-cellulose with a quantity of H_2S sufficient for decomposing the SO_2 present. The sulphur is nearly completely precipitated in the colloid state; after removing it, the liquid may be utilised for other purposes.

W. A. Hall (B. P. 20760 of 1912) prepares sulphur from a mixture of equal molecules of H_2S and SO_2 by passing it, Page 48. *Estimation of the degree of Fineness of Ground Sulphur by Chancel's Sulphurimeter.*—The Swiss Union of Analytical Chemists (*Z. anal. Chem.*, 1906, xlv. p. 760) recommends the following way of proceeding for testing the degree of fineness of the sulphur, intended for viticultural purposes, by means of Chancel's sulphurimeter. Five g. taken from a larger sample of brimstone, passed through a 2-mm. wire sieve, are introduced into the sulphurimeter by means of a small funnel, the neck of which has been removed, with the assistance of a glass rod and a hair brush. The sulphur adhering to the funnel, glass rod, and brush is rinsed off with ether. After the air has been driven out of the apparatus, it is filled up to the mark 100 by ether, closed by its glass stopper, and placed for a short time into water of 17·5° C. Now the contents of the tube (which is best wrapped in a woollen cloth) are thoroughly mixed during one minute by vigorous, long pushes in the longitudinal direction; the sulphurimeter is then quickly placed in a stand in a vertical position, any further shaking is avoided, and the place up to which the sulphur reaches is read off. This operation is repeated ten times, and the mean result taken. The following points are observed for a judgment of the quality:—

1. Sulphur samples with more than 2 per mille of mineral admixtures are to be designated as impure.

2. For sublimed sulphur 40°, for ground sulphur 60°, for blown sulphur 70° Chancel, must be demanded.

3. Under the microscope the particles of the ground or blown sulphur appear angular and sharp-edged, those of sublimed sulphur rounded, smooth, and frequently cohering by fusion in rows. In the polarised light the former are translucent, the latter transparent. Pure ground sulphur is entirely soluble in carbon disulphide, sublimed sulphur only partially so. The following prescription, founded on Dusserre's proposals, serves

8° and 21°, and averages 13° Chancel.

The same Union recommends the following rules for estimating the sulphur in mixtures, especially those intended for dusting on grape-vines: If the sulphur is ground, and there are no other substances present which are soluble in carbon disulphide, the sample is extracted by carbon disulphide in a Soxhlet apparatus. If the sample contains sublimed sulphur, the following method (worked out by Dusserre) usually yields the desired result, on the supposition that there are no substances present which are insoluble in water, alcohol, and ether, and which are volatile. Ten g. of the powder are gradually mixed with so much dilute hydrochloric acid that the copper salts, lime, sodium carbonate, etc., are dissolved. Then filter, through asbestos, wash several times by cold water, then by alcohol, and lastly by a little ether, whereby soap, rosin, etc., are removed. The residue remaining on the asbestos filter, which contains only sulphur and the insoluble portions of the powder (talcum, china clay, etc.), is placed in a platinum crucible, dried in a water oven, weighed, ignited, and reweighed. The difference between the two weighings indicates the percentage of sulphur.

Opinions differ very much on the point whether ground crude sulphur or flowers of sulphur are to be preferred for dusting the vines. Fresenius and Beck prefer ground sulphur, because the crystalline powder of crude sulphur adheres on the leaves better than the amorphous flowers of sulphur. But in France the latter are considered as superior, because the division of the sulphur is much better than in ground sulphur (which is certainly mostly preferred, on account of its lower price), and because the acids adhering to the flowers contribute very efficiently to the destruction of the oïdium.

Urban (*Chem. Zentr.*, 1913, ii. p. 713) discusses the action of flowers of sulphur on the growth of sugar-beet.

Ger. P. 196371 of the Sachsenberger Aktien-Maschinenfabrik and Eisengiesserei.

Page 50. *Special Technical Forms of Sulphur.*—The Thomsen Chemical Company (Ger. P. 273761) prepare sulphur in such a form that, when suspended in water or other liquids, it is not coagulated by sulphuric acid, by grinding it to an extremely fine state, together with a colloid, *e.g.*, 50 parts sulphur with a solution of 5 parts glue in 50 water. Other suitable colloids are: extract of soap-bark, Irish moss, gum tragacanth or gum-arabic; or by grinding the sulphur in the dry state with the colloid and then with water. The product thus obtained serves for wetting shrubs, for destroying fungi, and (with addition of plumbic arseniate) for destroying insects.

"*Plastic*" *sulphur*, for employment in agriculture and viticulture, is made by Imbert (Fr. P. 459534) by adding 0·5 part ox-gall to 999·5 sulphur.

"*Precipitated*" *sulphur*, as sold for dealing with the vine disease, according to Kulisch (*Z. angew. Chem.*, 1914, ii. p. 415), has nothing to do with the precipitated sulphur used in pharmacy, and evidently comes from the coal-gas manufacture. It is a brown or black powder, containing 50 per cent. ashes (20 per cent. of which is ferric oxide), and only 33 per cent. real sulphur.

Leather-tanning by Precipitated Sulphur.—According to Apostolo (*Ann. Chim. anal.*, 1914, i. p. 124), instead of precipitating the sulphur on the leather from sodium thiosulphate by the addition of acids, the leather may be dipped in a liquid containing the sulphur precipitated from thiosulphate by the gradual addition of an acid in a state of suspense. After ten or twelve hours' treatment, white, very soft leather is obtained, holding for 100 parts from 2·5 to 3·5 parts of sulphur in a state of adsorption, and stable in warm, but not in cold water.

Page 51. *Colloidal Sulphur.*—Sarason (Ger. Ps. 216824 and colloidal way.

Julius Meyer (*Berl. Ber.*, 1913, p. 3089) prepares colloidal solutions of sulphur (or selenium) by dissolving ground sulphur (or selenium) in a few cubic centimetres of Kahlbaum's hydrazin sulphate up to saturation, by shaking, and pouring a few drops of the solution, rapidly shaking, into several litres of water. In the case of sulphur this proceeding yields a solution which has at first a lemon-yellow, later on through formation of colloidal sulphur a yellowish white colour, and which is not very stable nor dialysable.

Application of Colloidal Sulphur.—Lumière and Seyewetz (*Ball. soc. franç.*, 1912, p. 375) apply it for "toning" solutions of silver bromide for photographic purposes. The photographs are soaked in a solution of 125 g. "fixating soda" in 1 litre water, to which had been added 250 c.c. 50-per-cent. dextrine solution and, shortly before use, 50 c.c. hydrochloric acid. The photographs remain in this solution for twenty to twenty-five minutes and are then washed one and a half hours, whereby the toning process is completed. In this treatment the white places remain quite intact.

Analytical Methods for Commercial Brimstone.

Page 51. *Estimation of the Moisture in Commercial Brimstone.*—In the case of unground brimstone it is frequently unnecessary to estimate the moisture, but this may be necessary in cases of wetting on purpose, or of accidental exposure to rain. It is not as simple an operation as it looks, since it is hardly possible to obtain a sample representing the real average of moisture, and still less possible to preserve the sample without loss of moisture, as far as it is required for the laboratory use. In the case of coarse sulphur the sample must be crushed as quickly as possible, only quite coarsely, and at least 100 g. must be employed for the estimation of moisture. In

Estimation of Free Sulphur in Commercial Brimstone.—Berger (*Comptes rend.*, cxliii. p. 1160) pours 10 c.c. of fuming nitric acid over 0·1 to 0·2 g. of the substance, adds 0·5 to 1·0 g. potassium bromide, allows to stand for a few minutes, evaporates to dryness, treats the residue a few times by hydrochloric acid, takes it up with water, and estimates the sulphuric acid formed by precipitation with barium chloride.

Page 52. *Analysis of Crude Sulphur.*—M. G. Levi (*Ann. Chim. anal.*, 1915, pp. 9-31; *J. Soc. Chem. Ind.*, 1915, p. 282) examined the methods proposed for estimating the sulphur in crude brimstone, especially in Sicilian sulphur containing bituminous impurities. The method of Carius did not yield exact results, no more than the combustion in a current of oxygen, which is quite suitable for purer forms of sulphur. Better results were obtained by the method of Fresenius and Beck (*Z. anal. Chem.*, xlii. p. 21), viz.: heating 10 g. a little over 200°, in order to volatilise the sulphur, weighing the residue and estimating the bitumen contained therein by reducing it to ashes. Exact results are obtained by means of nitric acid and bromine when proceeding in the following way. Place 0·2 g. of the sulphur in a 100 c.c. flask, connected by a ground-glass stopper with a reflux cooler, place the flask in an inclined position in cold water, and introduce 10 c.c. fuming sulphuric acid (sp. gr. 1·52) and then 5 drops bromine through the reflux tube. Shake the flask from time to time, until most of the sulphur and of the bromine is dissolved, add another 5 c.c. nitric acid, heat on the water-bath for half an hour, dip the flask into cold water, add 50 c.c. of water in small portions through the reflux tube, and precipitate the sulphuric acid formed as barium sulphate in the well-known way. In the case of low-grade crude sulphur, the sulphur must be extracted from the sample by carbon disulphide and then tested as above.

of Gas-works.—The process of Zulkowsky, which serves for this purpose as well as for pyrites, is described later on, in connection with the latter. So is that of Dennstedt.

Davis (*Chem. News*, xxxvi. p. 190) burns the spent oxide by heating in a current of air, passes the gases into a titrated solution of iodine, where the SO_2 is oxidised, and retitrates the excess of iodine by sodium thiosulphate.

Pfeiffer (*J. Gasbeleucht.*, xlviii p. 977) burns 1 g. of the sample in a flask, holding 5½ litres, filled with oxygen, in which 25 to 50 c.c. of normal caustic-soda solution had been placed. For this purpose the substance is put into an asbestos cup, formed from a wet, round sheet of asbestos, about 35 mm. diameter; this cup is held by a thick copper wire passing through the rubber stopper by which the flask is closed. The combustion is started by a small piece of glowing tinder, promoting it in case of need by putting on a little glycerine. When the combustion is finished, half an hour is allowed for the absorption of the gases; in order to oxidise the sulphide, 1 c.c. of 30-per-cent. neutral Merck's hydrogen-peroxide solution is added, and the excess of NaOH titrated back in the flask itself by means of normal acid and methyl-orange. Each cubic centimetre of the caustic-soda solution is = 1·6035 per cent. S.

Somerville burns the sulphur of the spent oxide in a current of oxygen, absorbs the SO_2 in caustic-soda solution, oxidises it by hydrogen peroxide, and estimates the sulphuric acid by precipitation with barium chloride, or by titration.

Espenhahn (*J. Soc. Chem. Ind.*, 1916, xxxv. p. 292) estimates the sulphur in the spent oxide by heating 0·4—0·7 g. of the finely powdered and washed material with 4 g. of reduced iron in a hard-glass crucible, whereby it is completely converted, after keeping for seven to ten minutes at dull red heat, into ferrous sulphate. After cooling in an atmosphere of carbon being thereby likewise converted into ferrous sulphide, which is estimated by decomposing with hydrochloric acid as above described.

We here give some details on the process of Davis and Foucar for the estimation of free sulphur in spent oxide, briefly mentioned in the text (p. 52). One g. of the finely ground (50 mesh) sample (or its equivalent, if previously dried) is dried in the water-bath for an hour (if not already dry), and then transferred to a 250 c.c. flask; 1·5 g. of sodium cyanide and 50 c.c. of absolute alcohol are added, and the contents are boiled under reflux for two hours. The alcohol is then completely removed by distillation, 100 c.c. of hot water added, and the solution washed into a 250 c.c. flask. The volume is made up to the mark, in the cold. To 25 c.c. of this solution 75 c.c. of water and 5 c.c. of saturated iron alum solution are added. The mixture is heated with constant stirring to 95°, filtered into a 750 c.c. beaker, and washed free from thiocyanate. When cool, 5 c.c. of nitric acid are added, the solution made up, if necessary, to 500 c.c. with water, and titrated with *N*/20 silver nitrate solution until the red colour of the ferric thiocyanate completely disappears; or an excess of silver nitrate may be added, and the solution titrated back with *N*/20 thiocyanate. Should the sample contain thiocyanate, as is most likely in the case of spent oxide, a blank test should be conducted, the thiocyanate being extracted with water. Should it be required to ascertain the amount of matter, other than sulphur, soluble in carbon disulphide, it may be determined by subtracting the sulphur content, found as above, from the figure obtained in the usual way for the percentage soluble in carbon disulphide.

Page 53. *Arsenic in brimstone* occurs mostly in the shape of As_2S_3, but sometimes also partly as As_2O_3, or, exceptionally, as calcium or ferric arsenite.

potassium iodide, and the whole is boiled, in order to complete the precipitation of the selenium and to convert it into the grey modification. The free iodine is removed by boiling with bisulphite, and the selenium filtered off through a Gooch crucible. If any tellurium is present, this is separated by dissolving the selenium in nitric acid, evaporating and precipitating with ammonia.

The method of Klason and Mellquist will be described later on, in connection with the description of the estimation of selenium in pyrites.

PYRITES.

Page 60. *A new iron disulphide* has been described by Doss, by the name of "melnikowite" (*Z. f. prakt. Geol.*, xx. pp. 453-482; *Chem Zentr.*, 1913, i. p. 737).

The influence of pyrites on the oxidation of coal is discussed by Drakeley (*J. Soc. Chem. Ind.*, cix. p. 723).

Page 64. Pyritic nodules with nuclei of carbon have been found in the oasis of Kargeh in Egypt (*Chem. News*, 1916, cxiv. p. 34).

Page 66. *Production of Pyrites in Great Britain and Ireland*:

In 1910 . .	9,380 tons.
1911 . .	10,114 „
1912 . .	10,552 „
In 1913 . .	11,427 tons.
1914 . .	11,654 „

Importation of pyrites into Great Britain in 1910, 810,000 tons; in 1911, 849 921 tons.

In 1915 the production was 394,124 long tons; the consumption 1,358,768 tons.

Page 69. *Production and Importation of Pyrites in Germany*:

Year.	Production.	Importation (deducting the quantities exported).

Consumption of pyrites in Germany, 1913, 915,265 tons; of which 105,741 was produced at home and 810,524 imported.

Austria-Hungary:

Year.	Produced.	Imported.	Exported.
	Tons.	Tons.	Tons.
1910	92,464	...	...
1911	100,000	150,000	...
1912	...	186,090	5,081
1913	...	130,526	3,885

Page 74. *Production of Pyrites in France;*

In 1910 . . 250,432 tons. In 1911 . . 240,000 tons.

Importation of Pyrites into France:

Year.	Tons.	Year.	Tons.
1900	92,000	1908	307,000
1905	251,000	1909	235,000
1906	364,000	1910	270,000
1907	331,000	1911	450,000

The exportation since 1900 has been *nil.*

Page 77. *Pyrites in Russia.*—Production in 1910, 50,000 tons.

In 1911 there was imported 115,000 tons.

In 1912 Russia produced 130,000 tons and imported 145,000 tons pyrites; the consumption was 256,000 tons.

According to *Chem. Tr. J.*, 1915, p. 489, two beds of cupreous pyrites have been discovered 18 miles from Elisavetpol, one of which is already worked and yields per day 16 tons ore of 48 to 53 per cent. sulphur, which goes to the factories at Baku.

The San Domingo mines in Portugal furnish about 400,000 tons cupreous pyrites per annum, of which about 100,000 tons are exported to England, 100,000 tons to the United States, 100,000 elsewhere. The sulphur contents of that ore is about 50 per cent.; the copper contents, 0·5 per cent.; of zinc, lead, and arsenic, only traces (*Chem. Ind.*, 1914, p. 641).

Page 75. *Production of Pyrites in Italy.*—In the year 1911, 170,000 tons; in 1912, 248,612 tons non-cupreous and 28,973 tons cupreous pyrites; in 1913, 292,077 non-cupreous and 25,257 tons cupreous pyrites.

Importation.—In 1911, 115,000 tons.

Sweden.—Imported in 1911, 101300 tons pyrites (besides 34,622 tons crude sulphur). Its own production in 1910 was 25,445 tons; in 1911, 21,592 tons. In 1912 the importation was 155,000 tons and the home production 35,000 tons.

Pyrites in Norway.—This country exports ore containing 1 or 2 per cent. copper and 42 to 49 per cent. sulphur. The amount exported was :—

	Metric tons.		Metric tons.
In 1901 . .	101,900	In 1908 . .	251,500
1902 . .	121,200	1909 . .	282,606
1903 . .	129,900	1910 . .	322,000
1904 . .	133,500	1911 . .	350,000
1905 . .	161,000	1913 . .	390,000
1906 . .	194,500	1914 . .	358,114
1907 . .	234,500		

The production of pyrites in Norway in 1914 was about 430,000 tons, 358,114 tons of which was exported.

Sebelien, in *Chem. Zeit.*, 1914, p. 1119, makes detailed statements on the pyrites industry in Norway, of which we give a short abstract. The Foldalens Verk produces pyrites, containing on an average 1·85 per

Meldalen, some of which have been worked since the 17th century for copper, of which the washed pyrites contains from 5 to 8 per cent. The Röstvangen Co. has pits at a height of 950 to 1300 metres above the sea-level; the pyrites has been worked since 1908. That which is exported contains 2·4 to 3·4 per cent. copper, 42 to 46 per cent. sulphur; and, per ton, 0·3 to 2·0 g. Au and 10 to 80 g. Ag.

Falkenberg (*Zsch. prakt. Geol.*, 1914, p. 105) discusses in detail the geology and petrography of the pyrites beds in South Norway.

Page 84. *Pyrites in the United States.*—The production of pyrites (according to official statements) was in 1912, 350,928 tons; in 1913, 341,338 tons; in 1914, 336,662 tons.

There was imported in 1912, 970,785 tons; in 1913, 850,592 tons; in 1914, 1,026,017 tons. In 1915 the production was 394,124, the importation 964,634 tons, the consumption 1,358,768 long tons.

Detailed statements on the production and importation of pyrites are made in the *U.S. Min. Res.*, 1914, ii. pp. 140 *et seq.*

Page 85. *Pyrites in Canada.*—Production in 1910 50,000 tons; in 1911. 43,544 tons; in 1912, 79,700 tons; in 1913, 158,566 tons; in 1914, 224,958 tons; in 1915, 296,910 tons.

A special pamphlet on pyrites in Canada has been published by A. W. G. Wilson in 1912, at Ottawa.

Hopkins (*Bull. Am. Inst. Min. Eng.*, 1916, p. 1361) describes the pyrites deposits in South-Eastern Ontario. The ore mined averages 40 per cent. sulphur.

Exportation in 1908, 60,000; in 1909, 57,000; in 1910, 80,000; in 1911, 100,000 tons.

Pyrites in China.—In the province Chan-Si, which borders

Canada	48,098	73,809	72,791	141.577
United States	241,612	301,458	350,928	341,338
Belgium	211	120	146	264
Bosnia and Herzegovina	56	3,069	6,118	7.580
France	246,488	273,565	277.758	306,267
German Empire	212 311	214,034	258,517	224,808[1]
Greece	32 767	35,390	29,294	(?)
Hungary	91.008	95,231	102,174	104,950
Italy	133,492	143,823	244,097	287.777
Norway	324,457	363 243	457,014	434,342
Portugal	289,119	272,869	333,756	371 588
Russia	55,062	(?)	(?)	(?)
Servia	36,255	(?)	45.462	(?)
Spain	289.551	339,448	414,438	912,316
Sweden	25,044	29,622	31,334	33,779
Turkey	148,130	104,823	121,260	(?)
United Kingdom of Gt. Britain	9,380	10,114	10,522	11,427
Japan	78,421	72,585	74,594	(?)
Australia	2,916	2,496	(?)	(?)
Total	2,264,378	2,335,699	2,830,803	3,177,713
Sulphur displaced (on the assumption of 45 per cent. of sulphur content)	1,018,970	1,051,065	1,273,861	1,429 971

[1] Prussia only.

Page 89. *Proportional Value of Poor and Rich Pyrites.*—A discussion on this point has been carried on by Keppeler, Nemes, and Uhlmann in *Chem. Zeit.*, 1912, p. 1219; 1913, pp. 2, 59, 318; 1914, pp. 597, 816. Keppeler describes comparative roasting trials with Spanish pyrites-smalls, containing 48·4 per cent. sulphur, and Norwegian smalls, containing 43·28 per cent. sulphur, and more copper and zinc sulphide than the former. They were roasted in mechanical dust-burners with three floors. Of the Norwegian ore less sulphur could be worked, and the utilisation of the sulphur was less perfect that with Spanish ore. Of the poorer ore less sulphur can be burned in the same time than of the richer ore, and the roasting is less complete with the former than with the latter. Therefore equal quantities of sulphur have a smaller value in the ore with the modern burners is more economical than that of the richer ore. The same contention is made by Uhlmann, who also states that the acid produced by the poorer ore contains less arsenic than that made from the richer ore. Keppeler contradicts this, and asserts that the results obtained with the various descriptions of pyrites depend upon the system of burner used. Uhlmann, again, contends that in ordinary chambers in the long run the same quantity of acid can be made with Norwegian as with Spanish ore. The temperature on the third floor of the burners must be kept high; on the fourth and fifth floors hardly any combustion, only a cooling of the cinders, takes place. Considering the easy working of the Norwegian ore, its freedom from arsenic, and the small production of dust, it may be considered rather more valuable than the Spanish ore. Albrecht also contends that of all known descriptions of pyrites, the Norwegian ores are burned in the best and easiest way; only an ore of Turkish origin was equal to them.

Page 89. *Analysis of Pyrites.*—A very large amount of work has been recently done in this direction by a great number of chemists. That which had been published up to 1908 is embodied in the respective chapter of Lunge's *Technical Methods of Chemical Analysis*, edited by C. A. Keane, Vol. I., pp. 272 *et seq.*; and, more briefly, in Lunge's *Technical Chemists' Handbook*, 1916, pp. 108 *et seq.* We here quote such matter as is not contained in the text of Vol. I. of *Sulphuric Acid and Alkali*, pp. 89 *et seq.*

Estimation of Moisture.—Dry the coarsely ground sample at 105° until the weight remains constant. For the other tests the pyrites is not employed in the dried state, but directly in the finely ground sample, kept in a well-sealed bottle. The opposite error, caused by the slight solubility of barium sulphate in the hot solution, containing free HCl and ammonium chloride. (This disposes of the objection made by H. C. Moore in *J. Ind. Eng. Chem.*, 1915, p. 634.)

Smoot (*Eng. and Min. J.*, 1912, p. 412) and Berthiaux (*Ann. Chim. anal.*, xviii. p. 468) remove the iron electrolytically before the precipitation by barium chloride, but this offers no advantage against Lunge's method (precipitation by ammonia as described in the text).

The *dry* methods of decomposing pyrites, described by several chemists (*e.g.*, Fresenius, in *Z. anal. Chem.*, 1877, p. 335, Boeckmann, Pelouze, and others), in the case of testing pyrites, offer no advantage over Lunge's methods, but are more liable to cause errors. They are better adapted to estimating the sulphur left in pyrites cinders.

Other methods for estimating Sulphuric Acid.—Silberberger (*Ber.*, 1903, pp. 2755 and 4259) recommends precipitating the sulphuric acid by strontium chloride in an alcoholic solution, which according to his assertion produces precipitates free from chlorine and iron, especially in the analysis of pyrites. An examination of this method by Lunge (*Z. angew. Chem.*, 1904, pp. 913, 949; 1905, p. 449) has shown that this method must be rejected, since the filtration is extremely slow and yields muddy filtrates, and the behaviour of strontium sulphate on ignition is troublesome.

Tarugi and Bianchi (*Chem. Zentr.*, 1906, ii. p. 708) describe an apparatus in which the barium sulphate is made to ascend in a narrow tube, where the liquid clarifies at once, and can be tested by adding barium chloride. The same process is described by Lang and Allen (*J. Chem. Soc.*, 1907, p. 1370).

Borgi and Sotgia (*Abst. Amer. Chem. Soc.*, 1916, p. 1308) modify the method of Andrews, described in the text, of precipitating the sulphuric acid by a solution of barium chromate

Grossman (*Chem. News*, 1880, p. 114).
Telle (*Chem. Centr.*, 1898, p. 218).
Scholtz (*Arch. Pharm.*, 1905, p. 667).
W. J. Müller (*Ber.*, 1902, p. 1587).
Müller and Dürkes (*Z. anal. Chem.*, 1903, p. 477).
Raschig (*Z. angew. Chem.*, 1903, pp. 617 and 818; 1906, p. 332).
Knorre (*Chem. Ind.*, 1905, p. 2).
Friedheim and Nydegger (*Z. angew. Chem.*, 1907, p. 9).
Nickel (*ibid.*, 1910, p. 1560).
Zehetmayr (*ibid.*, 1910, p. 1359).
Hassreidter and van Zuylen (*Chem. Zentr.*, 1905, i. p. 1433).

Page 101. *Estimation of the available Sulphur in Spent Oxide of Gas-works.*—As an improvement on Zulkowsky's method, described in the text (p. 101), it is recommended to pass the gases, not through a solution of potassium hypobromite solution, but through a solution of hydrogen peroxide, and to estimate the sulphuric acid formed in this solution by titration with sodium hydrate or carbonate, deducting the acid previously present in the hydrogen peroxide. The last operation is unnecessary when employing Merck's pure, neutral hydrogen peroxide. The reaction is:

$$H_2O_2 + SO_2 + H_2SO_4.$$

Page 102. *Estimation of the available Sulphur in Pyrites (or Gas-sulphur).*—Objections have been raised against the method of Zulkowsky, described in our text, p. 101, by Dennstedt and Hassler (*Z. angew. Chem.*, 1905, pp. 1134 and 1562; 1906, p. 1668). To begin with, they employ, in lieu of platinised asbestos (which retains some sulphuric acid), platinised quartz, and absorb the sulphuric acid by dry lead peroxide or sodium of in a non-transparent quartz tube, in a transparent tube of fused rock-crystal. The oxygen is passed through strong sulphuric acid and introduced into the crystal tube by means of a ground tube, consisting of quartz glass, since ordinary glass, owing to its greater coefficient of expansion, would cause the crystal tube to burst. The other end of the crystal tube is drawn out conically for a length of 7 cm.; and an elbow tube of quartz glass, 5 mm. wide inside, is ground on. The ground places, in order to make the joints tight and to admit of being more easily taken to pieces, are rubbed in with fine graphite powder. The descending limb of the elbow tube is attached in an air-tight way to the large bulb of a ten-bulb tube. Between the large and the small bulbs a horizontal tube, 5 cm. long, is interposed, to which are joined two larger bulbs with a drop-catcher, in order to prevent the drawing-up of the bromine contained in the horizontal part of the tube. To the ten-bulb tube is attached a Peligot tube, and to this a Volhard's bulb flask. The absorbing liquid is bromine water, free from sulphate, the excess of which is easily driven off. Moreover, 2 c.c. pure bromine is put into the large bulb; it collects in the horizontal tube, and there instantaneously oxidises the sulphur dioxide. The Peligot tube is charged with bromine water, the Volhard flask with pure caustic-soda solution, to retain the bromine vapours; last comes a beaker containing pure water. The pyrites is placed in a thin porcelain boat, which is introduced in that part of the quartz tube which is near the drawn-out end. The test is commenced by starting the current of oxygen in such manner that two or three bubbles per second pass through the sulphuric-acid bottle. Then the boat containing the substance is heated, first only that end of the boat which is nearer the absorbing-apparatus, by the full flame of a Bunsen burner. When the heating the boat, the SO_2 and SO_3 formed are taken up by the bromine water and the bromine, which is decolorised by the SO_2. When the reaction slackens, more heat is applied; in the end, when no more glowing takes place, the part in front of the boat is strongly heated by a Teclu burner; lastly, also, the ground-in place at the reduced end of the first part of the elbow-pipe, which in the case of quartz tubes can be done without danger. The apparatus is now allowed to cool down, passing oxygen through all along, and is then taken to pieces. The elbow-tube is rinsed out with water, the liquids in the receivers (except the contents of the Volhard flask) are put into a beaker and heated on a water-bath until the brown colour of the bromine has gone away. Lastly, a few drops of alcohol are added; the liquid is heated to boiling for a short time, in order to destroy any persulphuric acid, and, if necessary, evaporated to 300 to 400 c.c. It is then neutralised by ammonia, after adding a little methyl-orange; 1 c.c. strong hydrochloric acid is added, and then the approximately calculated quantity of 1 per cent. barium-chloride solution, all at once. The barium sulphate is filtered in the usual way and weighed. The boat with the residue is first heated in a shallow capsule with strong sulphuric acid until dissolved, evaporated to dryness, the residue taken up with strong hydrochloric acid and hot water, and the gangue determined by filtering, washing by hydrochloric acid, and calcining in a platinum crucible. If its colour is not white or grey, but reddish or brown, the iron is removed from it by heating with concentrated hydrochloric acid, filtering, washing and again calcining. The filtrates must always be tested for any SO_4 ions. Each test requires altogether about one and a half hours. *E.g.*, four analyses of a sample of pyrites yielded 51·30, 51·03, 51·04, 51·00 per cent. sulphur.

and filtered. Two hundred c.c. of the filtrate is diluted to 450 c.c., 1 c.c. hydrochloric acid added, and the sulphuric acid precipitated by barium chloride in the usual manner. The presence of barium sulphate or silica in the cinder has no appreciable influence on the results obtained.

Page 106. *Estimation of Copper in Pyrites.*—The Duisburg copper works employ the following process:—Five g. of pyrites, ground and dried at 100°, are gradually dissolved in 50 c.c. nitric acid (sp. gr. 1·2) in an inclined Erlenmeyer flask. As soon as the violence of the reaction is over, the flask is warmed and evaporation allowed to proceed until sulphuric-acid vapours are given off. The dry residue is dissolved in 50 c.c. hydrochloric acid (sp. gr. 1·19), and after the addition of sodium hypophosphite (2 g. NaH_2PO_2 dissolved in 5 c.c. water) the solution is boiled for a time to remove arsenic, and to reduce the ferric to ferrous chloride. An excess of strong hydrochloric acid is then added, the solution diluted with about 300 c.c. hot water, hydrogen sulphide passed in, and the precipitate filtered off and thoroughly washed. A hole is made in the filter by means of a glass rod, the precipitate is washed back into the precipitating flask, and the metallic sulphides adhering to the filter paper, as well as the main bulk of precipitates, are brought into solution by treatment with nitric acid. The solution in the flask is then evaporated to dryness on the water-bath; the residue is again taken up by nitric acid and water, neutralised by ammonia, and dilute sulphuric acid is added in slight excess. When cold, the solution is filtered in order to remove any lead sulphate and other insoluble matter; the flask and the filter are washed by water containing sulphuric acid; 3 to 8 c.c. of nitric acid of sp. gr. 1·4 are added to the filtrate, and the copper is deposited electrolytically. From the acid and precipitates the copper as cuprous thiocyanate; this is oxidised by a mixture of sulphuric and nitric acids to sulphate, and the copper determined by electrolysis. Electrolytic methods for the estimation of copper in ores are also employed by Heidenreich (*Z. anal. Chem.*, 1901, p. 15) and Treadwell (*Chem. Zeit.*, 1912, p. 961).

A very complete account of the estimation of copper in pyrites, and more particularly also of the "Cornish assay" (*vide* our text, p. 79), is given by Westmoreland (*J. Soc. Chem. Ind.*, 1886, p. 49; criticised, *ibid.*, p. 277). We mention also the papers by L. and G. Campedon (*Stahl u. Eisen*, 1905, p. 542) and Reimen (*ibid.*, 1905, p. 1359).

Estimation of Lead in Pyrites.—The lead remains in the shape of sulphate in the residue from treating pyrites with aqua regia (*vide* the text, pp. 90 *et seq.*). It is extracted from that residue by heating this with a concentrated solution of ammonium acetate; this solution is evaporated, with addition of a little pure sulphuric acid, finally in a porcelain capsule, dried and ignited; 1 part $PbSO_4 = 0{\cdot}6831$ Pb.

Koch (*Chem. Zeit.*, 1908, p. 124) titrates the lead by sodium-sulphide solution. Low (*J. Amer. Chem. Soc.*, 1908, p. 587) dissolves the lead sulphate in sodium-acetate solution, converts it by addition of potassium bichromate into lead chromate, converts this by digestion with a hot solution of oxalic acid into oxalate, and titrates this by potassium permanganate.

Estimation of Zinc.—This is sometimes estimated in pyrites, because the sulphur combined with zinc is lost in the ordinary process of burning the pyrites. The method of Schaffner, described in Lunge's *Technical Methods of Chemical Analysis*, i. p. 289, and ii. p. 291) is not available in this case in its original shape, owing to the large preponderance of iron, but it can be employed if the iron is first removed by Rothe's in 10 c.c. hydrochloric acid (sp. gr. 1·105), dilute with a little water, precipitate lead, arsenic, and copper by hydrogen sulphide, and filter the sulphides off. Oxidise the solution, separated from the sulphides, in the boiling state by 2 or 3 c.c. nitric acid (sp. gr. 1·4), and transfer it into a 250 c.c. flask. After cooling, add 25 c.c. ammoniacal liquor (sp. gr. 0·915), fill up to the mark, shake up, filter, and employ 200 c.c. of the filtrate (corresponding to 1 g. of the substance), after dilution with 100 c.c. water, for titration by sodium-sulphide solution, of which each cubic centimetre indicates 0·005 g. zinc. This titration liquid is prepared in an analogous manner by dissolving a corresponding quantity of pure zinc in 5 c.c. hydrochloric acid of sp. gr. 1·19, adding 1 to 2 c.c. nitric acid, some water, and 25 c.c. ammoniacal liquor, filling up to 250 c.c., and titrating 200 c.c. of this mixture diluted with 200 c.c. water at the same time as the solution to be analysed.

Instead of this process the zinc can be estimated by gravimetric analysis. Dissolve 1 g. pyrites in aqua regia, as described on p. 90 of the text, evaporate off the excess of nitric acid, take up the residue by 5 c.c. strong hydrochloric acid, add water, and treat the solution with hydrogen sulphide to remove any metals yielding sulphides insoluble in the acid solution. Any precipitate formed is filtered off, the filtrate freed from H_2S by boiling, and oxidised by aqua regia. The oxidised solution, after cooling, is treated with ammonium carbonate until the resulting precipitate only redissolves very slowly; ammonium acetate is then added, the solution boiled for a short time, and filtered. The basic ferric acetate so precipitated carries down some of the zinc, and must therefore be dissolved in hydrochloric acid and again precipitated; the operation is repeated so long as any zinc can be detected in the filtrate. The combined filtrates are concentrated if necessary, and the free from H_2S, filtered, precipitated with carbonate, the zinc carbonate well washed, dried, and converted by ignition into ZnO, of which one part = 0·8034 Zn. For very exact determinations any silica, oxide of iron, and alumina precipitated with the zinc oxide must be estimated and allowed for; this, however, is seldom necessary.

Rubricius (*Chem. Zeit.*, 1915, p. 198) estimates small quantities of zinc in ores and pyrites cinders as follows:—Dissolve 5 g. of the ore in 15 c.c. concentrated hydrochloric acid, with application of heat, add a few cubic centimetres of concentrated nitric acid, evaporate to a small bulk (but not to dryness), allow to cool, and stir up with 30 c.c. concentrated ammonia solution. The precipitate is twice or three times treated by ammonia, filtered, and washed by hot water. If the filtrate does not by a blue coloration indicate the presence of copper, add a little cupric sulphate, heat to boiling, add a little sodium sulphide, filter off the precipitated sulphides, wash them with hot water, dissolve the ZnS by hot dilute hydrochloric acid, precipitate the zinc from the boiling solution, and weigh it as ZnO. If any manganese is present, this is removed from the mixture of sulphides by treatment with dilute acetic acid, previously to the treatment by hydrochloric acid.

Carbonates of the alkaline earths are occasionally estimated in pyrites as they retain sulphur, owing to the formation of the corresponding sulphates. Since their quantity is always very small, the CO_2 cannot be accurately estimated by loss, and consequently a direct method must be used. The CO_2 is liberated by addition of strong acid and absorbed in soda-lime, taking care to retain moisture and any acid carried forward. For this purpose the well-known apparatus of Fresenius or of Classen may be employed, but greater rapidity and accuracy two small U-tubes, each containing 3 c.c. of a solution of chromium trioxide in concentrated sulphuric acid. After leaving the U-tubes, the gas is passed through a tube filled with glass beads moistened with sulphuric acid, then through a couple of calcium-chloride tubes, and is finally absorbed in two weighed tubes filled with soda-lime.

Selenium.—The detection and estimation of selenium in pyrites is briefly mentioned on pp. 55 and 1072 of our text. The method of Klason has been more extensively described by Klason and Mellquist (*Ark. Kemi*, 1912, No. 29; *Z. angew. Chem.*, 1912, p. 514; *J. Chem. Soc. Abstr.*, 1912, ii. p. 201). According to them, both the acid from the Glover tower and the chamber acid may show a red colour, caused by colloidal selenium. Some of the selenium dust contained in the pyrites-burner gases is retained in the Glover tower, but most of it passes through the tower and is found in the chamber acid. In order to estimate the selenium in crude brimstone, this is burned in a current of oxygen, in a porcelain boat placed in a glass tube, 1 m. long, between two asbestos plugs, which retain the SeO_2 formed almost completely. The SeO_2 is several times sublimed backwards and forwards, till it has turned perfectly white; it is then dissolved out of the tube and the asbestos plugs by water. The solution is diluted to 100 to 300 c.c. in a flask, and then 2 to 10 drops of hydrochloric acid (sp. gr. 1·19) are added. The flask and its contents are heated on a water-bath, the air is replaced by CO_2, and 2 to 5 g. of potassium iodide is added. After well corking the flask, it is shaken to dissolve the iodide, cooled, and then kept in the dark for one hour. The iodine liberated by the reaction,

$$SeO_2 + 4HI = Se + 2H_2O + I_2,$$

is titrated with standard thiosulphate.

per ton.

For the estimation of selenium in pyrites, 20 to 30 g. of this are dissolved in hydrochloric acid (sp. gr. 1·19) and potassium chlorate. After filtering from the gangue, the iron is reduced to the ferrous state by means of zinc, more hydrochloric acid is added, the solution boiled, and the selenium precipitated by stannous chloride. Since it may contain arsenic, it is collected on an asbestos filter, dissolved in potassium iodide, and again precipitated by hydrochloric acid and sulphur dioxide. The further treatment is similar to that described *suprà*, for the estimation of selenium in sulphur. 89·5 to 90·1 g. of selenium per ton were found in some specimens of Falun pyrites.

A simple roasting of the pyrites in a current of oxygen does not convert all the selenium into dioxide. The examination of fourteen samples of pyrites showed great variations in the proportions between the selenium going away with the roasting-gases and that remaining in the pyrites cinders. If the pyrites contains copper or lead, much more selenium remains in the cinders than otherwise.

J. Meyer and W. von Gaon (*Z. anal. Chem.*, liii. p. 29) describe a colorimetric method for estimating minute quantities of selenium, and a method of titrating with thiosulphate for the estimation of more considerable quantities of selenium. J. Meyer (*ibid.*, p. 145) describes improvements of the gravimetric estimation of selenium. Gutbier and Engeloff (*ibid.*, iv. p. 193) describe the results they have obtained by these methods. Compare also Meunier, *Comptes rend.*, 1916, clxiii. p. 332.

Estimation of Arsenic in Pyrites.—We here give some details on the methods of Blattner and Brasseur (*Bull. Soc. Chim.*, 1897, xvii. p. 13), simply mentioned in the text, p. 108. They quote an instance in which different analysts found from 0·19 to slight precipitate of ferric hydroxide is formed, SO_2 passed through the cold solution until the reduction of the iron to the ferrous state is complete, the excess of SO_2 is removed by warming, and after cooling to 60° to 70°, the arsenic is precipitated by passing in H_2S for six or seven hours. The solution is then allowed to stand for twelve hours, and filtered. The precipitate is washed by water containing HCl and H_2S, until all the iron has been removed, and then by distilled water. It is then dissolved by digesting the precipitate and filter paper with ammonium carbonate, and the solution is filtered. The solution is strongly acidified by hydrochloric acid warmed to 50° to 70°, and the arsenic is precipitated as As_2S_3 by passing in H_2S for an hour. The arsenic in the precipitate may be determined either as magnesium-ammonium arsenate or as silver arsenate. In the former case the precipitate is dissolved in strong ammonia, evaporated to dryness on the water-bath, taken up with 10 c.c. nitric acid, and, after a slight evaporation, rendered ammoniacal, and a small quantity of alcohol, followed by magnesia mixture, is added. After standing for twelve hours, the precipitate is collected on an ash-free filter paper, washed by a solution of one part of ammonium chloride and one part of alcohol in three of water, dried, and ignited after separation from the filter paper. The filter paper is ignited separately after addition of a small quantity of ammonium nitrate. One hundred parts $Mg_2As_2O_7$ correspond to 48·28 parts As.

II. *Dry Treatment.*—Two g. pyrites are thoroughly mixed in a platinum crucible of 30 c.c. capacity with 10 to 12 g. of equal parts of potassium nitrate and sodium carbonate, and covered by a layer of 2 g. of the same mixture. The crucible is then covered, and heated over a Bunsen flame 3 cm. high. When the reaction is complete, the mass is allowed to cool, the heated to boiling, allowed to cool, rendered exactly neutral by ammonia, and, after the addition of one drop of nitric acid, again neutralised, until a drop of the solution produces a blue tint on red litmus paper only after some seconds. Silver nitrate is then added, drop by drop, until no further precipitation takes place; the silver arsenate is collected on a filter and washed with cold water, until the filtrate no longer gives a turbidity with hydrochloric acid. The silver arsenate is dissolved on the filter in very dilute nitric acid, 5 c.c. of an iron solution in sulphuric and nitric acid is added as indicator, and the solution titrated by *N*/10 ammonium-thiocyanate solution up to the appearance of a pink colour. Each c.c. of the thiocyanate solution corresponds to 0·0025 g. As. This method is rapid, and the results agree very closely with those obtained by the first method, and also with those of Clark, who employs a mixture of magnesia and sodium hydroxide for fusing the ore (*vide* our text, p. 107). The second method is preferable to the first, since in this arsenic may be lost by volatilisation of its chloride.

List (*Z. angew. Chem.*, 1903, p. 415) heats 2 g. pyrites with sodium peroxide, which transforms the arsenic into arsenic acid; this is estimated by the just described method of Blattner and Brasseur. Parr (*J. Amer. Chem. Soc.*, 1908, p. 764) also employs a sodium peroxide mixture.

Ebough and Sprague (*ibid.*, p. 1475) fuse pyrites with sodium carbonate and zinc oxide, acidulate the aqueous extract by acetic acid, precipitate the arsenic acid by silver nitrate, dissolve the silver arsenate in dilute nitric acid, and titrate it by ammonium or potassium sulphocyanate.

Low (*ibid.*, 1906, p. 1715) heats the ore with potassium bisulphate, tartaric acid, and concentrated sulphuric acid, precipitates from the solution the arsenic (and antimony) by H_2S, dissolves the sulphides in ammonium sulphide, and titrates by tons from Italy, 9477

Analysis.—Strontia has been found in blende to the extent of 0·05 to 4·8 per cent. SrO by Beyne (*Bull. Soc. Chim. Belg.*, 1913, p. 159). This must be taken account of in the estimation of the available sulphur.

The estimation of the *zinc* contents of blende does not concern the manufacture of sulphuric acid, but that of the zinc itself. The methods used for that purpose are described in Lunge-Keane's *Technical Methods of Chemical Analysis*, 1908, vol. i. pp. 289 *et seq.*

For the estimation of *sulphur* in zinc blende and roasted blende, Koelsch (*Chem. Zeit.*, 1916, p. 174) fuses 0·625 g. of blende, or 1·25 g. of roasted blende, with 15 g. sodium peroxide in an iron crucible. The cooled mass is dissolved in about 150 c.c. of water, the solution nearly neutralised by hydrochloric acid, diluted to 250 c.c., filtered, and the sulphuric acid estimated in 200 c.c. of the filtrate by precipitation as barium sulphate. The presence of a small quantity of silica in the ore does not appreciably affect the results. This process yields results coinciding with those obtained by fusing with potassium chlorate and sodium carbonates, and better results than the solution in aqua regia, which cannot be recommended, least of all for crude blende. The iron crucibles employed for the above-described process, of 2 mm. thickness of plate and a capacity of 25 c.c., stand about twenty-five fusings. They are best placed in iron triangles, stoneware triangles being quickly destroyed.

Page 120. *Use of Spent Oxide of Gas-works for the Manufacture of Sulphuric Acid.*—Koppers (B. P. 21385, 1913) exposes the spent oxide to the action of steam and gases at a temperature below that of the volatilisation of sulphur, in order to destroy the organic substance. The ammonia contained in

Fritzsche (Ger. Ps. 250243, 251353); Soc. H. Gouthrière (Ger. P. 245570); *Akt. Ges. f. chem. Industrie* and Wolf (Ger. P. 248001).

Ciselet and Deguide (Ger. P. 288767) dissolve the ferric hydrate by sulphuric or hydrochloric acid, leaving the free sulphur and the ferrocyanides behind and separating these in the well-known manner.

Espenhahn (*J. Soc. Chem. Ind.*, 1916, p. 292) describes the estimation free sulphur in spent oxide of gas-works (*vide suprà*, p. 22).

Page 122. *Use of Hydrogen Sulphide for the Production of Sulphuric Acid.*—The German patent for the process of Feld, mentioned in the text, is No. 237667.

Pintsch, Strache, and Hiller (Ger. P. 283601) cause the oxidation of hydrogen sulphide into sulphuric acid without any separation of free sulphur, by passing the gases containing H_2S into a hot solution of ferric sulphate, containing an excess of sulphuric acid, in which the regeneration of the ferric sulphate from the ferrous sulphate formed is brought about by air or oxygen, either at the same time or turn by turn. The sulphur separated in the first instance dissolves in the hot sulphuric acid, which is thereby partially reduced to sulphurous acid; the latter again reduces the ferric ion, being oxidised into sulphuric acid. The sulphuric acid made in this way contains iron; it can be used for most purposes, also for the absorption of ammonia, in which case, on reaching the point of neutralisation, the ferrous sulphide, which is now stable, is separated from the solution of ammonium sulphate, and is regenerated into sulphate by being again introduced into the oxidising solution.

NITRATE OF SODA.

50 cents (U.S.) per quintal (104·4 lb.).

A detailed description of the Chilian nitre industry is made by John G. Beck, in *Mining Press*, 1915, pp. 510 *et seq.*; by M. R. Lamb, in *Eng. and Min. Journ.*, 1915, pp. 811 *et seq.*; by Oesterreicher (*Prometheus*, 1915, p. 273).

The ordinary percentage of sodium nitrate in caliche is from 17 to 20 per cent. (not 48 to 75 per cent., as stated in the text).

Page 126. *An improved process for extracting the nitre from caliche* is described in the B. P. 23591, 1912, of Sulman, Picard, and Broadbridge.

According to *Min. and Eng. World*, 1915, p. 137, special efforts are being directed towards reducing the cost of mining sodium nitrate, which at present represents 60 per cent. of the cost of the raw product. One of the heaviest items of expense is the removal of the overburden, consisting generally of a hard mixture of sand and clay. In some cases this overburden is 20 ft. deep, making the cost of mining prohibitive. A large drag-line excavator has been installed at one field, and has given very satisfactory results in replacing hand labour. In the subsequent purification process of the caliche, the present evaporation process requires 1 lb. of fuel to produce 6 lb. of nitrate. A process has been patented by S. A. Orchard, by which it is claimed that 16 to 19 lb. of nitrate can be produced per pound of fuel; in this process the solution is passed through five or six evaporators, the first three or four of these working under vacuum, and the remainder under a slight steam pressure.

Effect of the European War on the Nitrate Industry.—Senor Enrique Cuevas, Conselor of the Chilian Embassy to the U.S.A., has made the following statement on the effect of the European War on the production and exports of Chilian more important consuming markets have been cut off, and the means of transportation considerably curtailed. These conditions influenced almost immediately the production of nitrate. Some *oficinas* closed down at once, but the greater number continued in operation during the month of August 1914. In September of the same year, the output showed a remarkable decrease, and of the 170 *oficinas* at work before the war, only 34 were active at the end of the year. The production, which had averaged about 5,000,000 quintals a month, fell to less than 2,000,000. The stocks on the coast, in August and September 1914, exceeded 1,100,000 tons, as a result of the heavy production in June and July, coupled with small shipments in August and September. Soon after the declaration of war, nitrate exports to Germany, Belgium, and very important districts of France ceased. Then again, the scarcity of bottoms, due to loss and internment of ships, has produced an enormous increase in freight rates. The ordinary freight rate from Chili to Europe before the war ranged from $6 to $7·50. As the war progressed, the rate rose and by degrees went up to $20, at which figure it remained for some time, only to rise again lately to $25 and even higher. The exports from July to December 1914 reached only 14,003,252 quintals; making a total for the year of 40,147,500 instead of 60,000,000 exported in 1913. During the first half of the present year (1915), the exportation was 18,067,462 quintals, while during the second half, with estimated figures for the months of November and December, it will amount to 22,600,000 quintals; making a total for the year of 40,067,462 quintals." (From the complete statistics brought up to date, it will be seen that this estimate was in fact exceeded by nearly 4,000,000 quintals.)

"Of course, the price for the consumer has likewise been affected, not only on account of the rise in freight rates, but also by reason of the speculation in the different markets due

1915, over 100 by October 1915, and 112 at the end of 1915.

The statistics of production are closely reflected in the price of the Chilian nitrate which, at the beginning of the war, was sold at about 6s. per quintal f.o.b. Chilian ports, falling to 5s. 9d. after the war had commenced, but rising to 9s. 3d. by October and November 1915; the present prices (October to November 1916) range about 9s.

Among the most important effects of the war on Chilian nitrates must be counted the prospective permanent competition of artificial nitrates, manufactured for competition with the products of the Chilian *oficinas* in every direction of their employment. It may be anticipated with confidence that the supply of nitrogen products from indigenous sources, in particular by utilising the nitrogen of the atmosphere, will be promoted by all leading military nations, in order to emancipate themselves, so far as possible, from Chilian supplies for the manufacture of munitions. The manufacture of nitrogen products as a link in the preparation of the nations for war will proceed without regard, at any rate primarily, to commercial conditions. The effect of these establishments, continuing or springing up afresh after the war, on the market prices of the various competing products cannot possibly be foreseen, since questions of public policy in keeping them alive and disposing of their output will necessarily introduce entirely artificial factors into the natural play of the law of supply and demand. The answer is comparatively simple, from the point of view of those who consider the future as belonging entirely to artificial products, manufactured under conditions with which, it is maintained, the Chilian nitrates cannot hope to compete economically, *i.e.*, where water power or coal are extremely cheap and conveniently available. On the other hand, it is pointed out, by progressive Chilian nitrate competition of artificial products; these sources are, a lower cost of production, improved methods of sale, and co-operation with the Chilian Government. The present cost price of Chilian nitrates in *cancha* (on the drying floor) ranges between 5s. and 7s. (including the Government duty) per quintal, according to local conditions. The minimum cost price under normal conditions is, according to reliable private information, about 2s. 6d. per quintal, to which the duty of 2s. 4d. has to be added. Improved methods of production, amongst which the utilisation of low-grade ore and the perfection of the plant are predominant, are anticipated to secure a reduction in the cost of production of 6d. per quintal, whilst a reduction by as much as 1s. is not beyond the range of possibility, in the light of expectations to which large-scale experiments are leading the investigators. The Government duty of 2s. 4d. per quintal will not readily be sacrificed, or even diminished, yielding, as it does, a proportion of the national revenue which the State cannot contemplate losing so long as it can by any means be kept alive. Yet, if that duty were to stand in the way of the continued existence of the Chilian nitrate industry, the Government would, as has been freely expressed in responsible Chilian quarters, prefer a fiscal system with an elastic duty, or an arrangement of profit-sharing, to the extermination of the industry and the nitrate revenue alike. Very important advantages are also expected to result from improved methods of distribution, and powerful voices advocate the creation of a combine on the lines of the German potash syndicate—the degree and manner of governmental control, if any, remaining a question open to many varying solutions. The realisation of the technical improvements which it is hoped to see resulting in the material lowering of the cost of production referred to, is a matter of the future, and the return to normal shipping nitrogen products in Europe. In order to appreciate the relevancy of such a reduction, it will be convenient to consider how close the market price of Chilian nitrate has run, say, sulphate of ammonia in recent years. Thus the average prices at Liverpool (calculated from the weekly listed prices) have been:—

Year.	Chilian nitrate. £	Sulphate of ammonia. £
1906	11	12
1907	11	11¾
1908	10	11¾
1909	9¾	11¼
1910	9½	12¼
1911	10	13¾
1912	11	14½
1913	11	13⅛
1914	10	11⅝
1915	12½	14½

Needless to say, the figure of £3, 10s. (which could only apply for the most favourably located *oficinas*) as a minimum to which the Chilian nitrates might descend in their struggle for existence in the European markets without entailing an absolute loss, is neither in near prospect nor independent of so revolutionary a step as a fusion of interests between the industry and the Chilian Government, who would have to face the temporary loss of their nitrate revenue to meet, under extreme conditions of competition, artificial products which could be marketed at correspondingly low rates. It is, however, not necessary to discount that extreme minimum in order to demonstrate that a purely commercial view of the manufacture of artificial nitrogen products will have to allow for a considerable competitive vitality of Chilian nitrate well below the ruling prices of recent years, and that the competition of the *oficinas*, technically improved, commercially co-ordinated, and reconciled with the interests of the Chilian Government, must impose necessary ultimate limits upon the scope of artificial cent. of the total area, have thus far been surveyed and their contents ascertained by excavations and test-holes. These 5811 sq. km. belong to the existing companies, private firms, and part of them are still in the hands of the Chilian Government. The estimated contents of these 5811 sq. km. were 290,300,000 tons of nitrate, of which up to the present 50,000,000 tons have been extracted, leaving in the surveyed portion of the area 240,300,000 tons of nitrate, equal at the present rate of production to a supply for an additional hundred years. The conclusion is drawn from the fact that the unexplored part is some thirty-four times larger than the grounds explored, that it is safe to estimate that it contains at least twice the quantity of nitrate of soda, and that consequently the nitrate zone in Chili can certainly provide nitrate of soda for another 300 years, at the present rate of production.

The quantity of nitrate of soda in the surveyed grounds is distributed as follows:—

	Tons remaining.
Tarapaca Province	33,000,000
Tocopilla District	27,000,000
Antofagasta (Central)	31,000,000
Antofagasta (Aguas Blancas District)	48,000,000
Taltal	93,000,000
Chanaral and Copiapo	8,000,000
Total	240,000,000

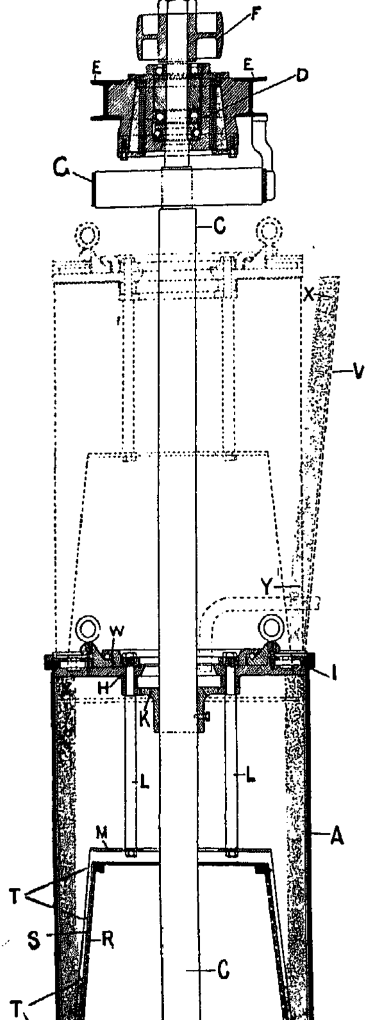
The Inspector-General of Nitrate Grounds, in his report to the Chilian Government, has arrived at these figures in the following manner:—In these surveyed grounds no raw material containing less than 17 per cent. of nitrate of soda has been taken into consideration, nor grounds where the thickness of the nitrate-bearing layer was less than 1 foot, except in the case of raw material with at least 25 per cent. of nitrate of soda, in which cases thickness of 8 in. or over has been being additional to the available workable supplies which, as stated above, are sufficient for 300 years at the present rate of exploitation.

Nitrate Exports from Chili.—The following figures have been courteously supplied by the Chilian Nitrate Committee in London, and may lay claim to high reliability. The amounts are stated in Spanish quintals, one quintal being equal to 101·44 pounds.

Years.	Spanish quintals.	Years.	Spanish quintals.
1830-1834	361,386	1890	23,373,000
1835-1839	761,349	1891	17,116,000
1840-1844	1,592,306	1892	17,478,000
1845-1849	2,060,592	1893	20,655,161
1850-1854	3,260,592	1894	23,947,014
1855-1859	5,638,763	1895	27,285,205
1860-1864	6,979,208	1896	25,175,832
1865-1869	10,594,026	1897	24,971,648
1869	2,507,000	1898	27,903.553
1870	2,943,000	1899	30,213,532
1871	3,606,000	1900	31,741,293
1872	4,421,000	1901	27,691,298
1873	6,264,000	1902	30,089,440
1874	5,583,000	1903	31,694,954
1875	7,191,000	1904	32,696,180
1876	7,035,000	1905	36,717,472
1877	4,522,000	1906	37,564,460
1878	5,909,000	1907	35,987,237
1879	2,065,000	1908	44,587,177
1880	2,496,000	1909	46,390,656
1881	4,590,000	1910	50,781,241
1882	8,242,000	1911	53,250,327
1883	10,768,000	1912	54,197,439
1884	10,513,000	1913	59,529,110
1885	10,797,000	1914	40,147,463
1886	9,805,000	1915	43,985,000
1887	15,495,000	1915 (July) to 1916	

Important improvements in the yield of nitrate have been effected by the installation of filtration plant specially adapted to the conditions of the *oficinas;* and according to a paper read by Mr J. Humberstone at the Mining Congress at Santiago (reported in the *South Pacific Mail* of 25th May 1916), the vacuum filters, so well known to the gold-mining industry, have proved capable of reducing the loss of material as well as the cost of production to a very material extent, besides rendering available in the future the enormous quantities of siftings and earth which now remain in the ground after extracting the upper crust, and which have not hitherto been utilised. Prolonged tests made on a large scale at the Agua Santa *oficina* have led the investigators to the definite conclusion that suitable methods of filtration rank foremost among the means of increasing the yield and reducing the cost of Chilian nitrates.

The treatment of the Chilian raw material has also been successfully dealt with by an apparatus which is introduced as a general substitute for filter presses and other filters by the Hydraulic Separating and Grading Co., Ltd., of 14 Queen Victoria Street, London. The apparatus is the invention of Mr W. J. Gee, and is patented in most industrial countries (B. P. No. 9365 of 1915). It is illustrated in sectional elevation in Fig. 1 and in cross-section in Fig. 2. In contrast to the ordinary leaf filter, in which the filtered solids accumulate on a cloth or other filtering material, this centrifugal filter always retains a clear filtering surface, and accordingly preserves throughout the maximum efficiency of the same. The machine consists of a cylindrical drum or outer shell, A, the diameter of which is about half the depth. This drum revolves at a high speed and is attached to a vertical spindle, C, running in ball bearings, D, of a special design (B. P. No. 16188 of



the drum. The vertical vanes and segmental plates surround a perforated cone, R, which is covered with a filter cloth or other suitable filtering material, so arranged as to be easily fixed and drawn tight or removed when required. The requisite speed, usually between 160 and 200 ft. per second peripheral velocity, being attained, the liquid containing the solid matter in suspension is fed in a steady stream through the hole in the middle of the cap, H, on to the distributor, K, and is at once thrown

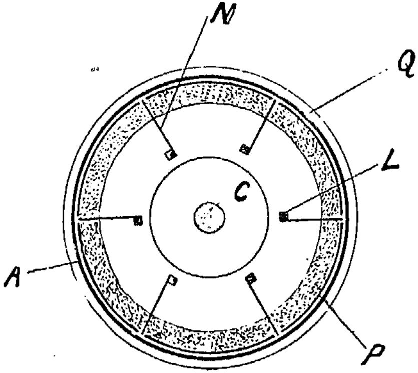


FIG. 2.

and thus a head of water is created which brings about a considerable pressure on the filtering surface. It is found that in most cases well over 90 per cent. of the solids never reach the filter at all, but are deposited by the centrifugal force on the drum. However, the liquid must pass through the filter, and such solid matter as is left in suspension is arrested on the surface of the filter, from which it is immediately thrown off by the centrifugal force and carried to the wall of the drum. It is found in practice that even particles of such fineness as will prohibit the employment of other filtering systems fail to choke the Gee centrifugal filter, in which the filtering material is invariably found clean throughout the operation and at the end. The charging is continued until a sufficient charge of deposits is recovered, the liquid passing out through the effluent holes, O. Then, after cutting off the feed for a short time, the rotation is continued until all the liquor contained in the drum has been thrown out, whilst the slabs of recovered solids are compacted and clear the lower end of the filter cone. The machine is then stopped and the structure embracing the inner parts within the drum drawn out, until it reaches the position shown by the dotted lines in Fig. 1, whereupon the plates with the recovered solids are simply lifted out, as shown at V, the solids adhering to the plates in a somewhat drier state than as recovered from the ordinary filter press. New plates are inserted, and the machine is restarted after a very short interruption. The wear and tear of filtering cloths is reduced practically to zero. On the plates the deposited solids are found graded, the coarsest and heaviest particles settling near the inlet at X, the finest at the outlet end near Y, with a range of all degrees of fineness between them; but this particular result of the operation, whilst of considerable importance in a number of industries, does not come into question in the manufacture of nitrate, where the solids deposited are not matter, and run it through towers or evaporate it in shallow vessels to dryness. The residual salt is dissolved in hot mother liquor from a previous operation, to obtain a solution saturated with nitrate at 120°, whereby most of the sodium chloride remains behind and is removed; the clear liquid is allowed to crystallise by cooling.

A. Schmidt (Ger. P. 243949) describes a lixiviating apparatus, which is specially adapted also to the treatment of crude nitre, consisting of a row of several vessels, provided with transportation spirals, by means of which the substance is moved on in a counter-current with the liquid.

Menge (in a pamphlet, published at Langensalza in 1914) describes the treatment of poor caliche by the process of Mourgues and Cortès, which consists in treating the clear aqueous solution with carbon dioxide and ammonia, whereby the mixture is converted into sodium bicarbonate and ammonium nitrate.

Gibb & Co., The Kestner Evaporating Co., Hobsbawn and Grigioni (B. P. 12474 of 1914) concentrate a solution containing sodium nitrate and chloride at ordinary atmosphere pressure up to a boiling-point of 123° or 124°, and keep it for some time at that temperature. This causes the sodium chloride to precipitate completely, and allows of separating it from the nitrate solution by settling and filtration.

The Norsk Hydroelektrisk Kvaelstof A.S. (Ger. P. 276814) describe a process for converting nitrate of soda into a fine powder adapted for fertilising purposes.

Page 126. *Other occurrences of Nitre.*—The nitre beds in Colorado are described by Headden in *J. Ind. Eng. Chem.*, Renson (*Chem. Trade J.*, 1913, p. 236) describes the nitre beds at Guayamango, in the Department of Ahuachapan in Salvador, where the nitre earth contains from 2·53 to 3·4 per cent. nitrate. The substance extracted therefrom contains many salts, and is so deliquescent that it cannot be carried in bags, unless previously mixed with quicklime.

A deposit of potassium nitrate has been discovered near Alpine, in Texas, according to the *Oil, Paint, and Drug Rep.* of 23rd Nov. 1914; others in Peru (*Z. angew. Chem.*, 1916, iii. p. 611), and in Ferghana (Russia) (*Chem. Ind.*, 1916, p. 437).

According to *Chem. Ind.*, 1916, p. 250, considerable beds of nitre, hitherto hardly utilised, exist in Persia (at the Urmia Lake, near Teheran, and near Kum), in Asia Minor (near Karabunar, south-east of Konia), and in the Vilayet Aleppo.

In 1916 the U.S. Geological Survey issued a Report stating that after two years' investigation of the nitrate deposits in the United States, none of importance had been found.

Page 128. *Statistics on Nitrate of Soda.*—W. Montgomery & Co. (*J. Soc. Chem. Ind.*, 1915, p. 27) make the following statements on the shipments and the consumption of nitrate of soda.

	1912.	1918.	1914.
	Tons.	Tons.	Tons.
Shipped from South American ports . .	2,456,000	2,647,000	2,660 000
Consumed in Great Britain	132,000	125,000	122,000
,, on the European Continent and in Egypt	1,711.000	1,689,000	1,868,000
,, in the United States . . .	503·800	583,000	553,000
,, in the whole world . . .	2,460,000	2,451,000	2,633,000

The consumption of nitrate of soda in Germany (*Chem. Trade J.*, 1916, p. 510) has been :

Production	2,783,440	2,471,351
Exportation to Europe and Egypt	2,028,426	1,240,085
„ „ the United States	633,404	541,787
„ „ other countries	87,411	72,170
Altogether	2,749,241	1,854,042
Visible stocks on 31st December	507,769	1,148,540

Ibid., 1916, iii. p. 102, it is reported that the Chilian nitrate industry has got into a very precarious state through the war. By the end of 1914 the Government had advanced already £900,000 against an interest of 7 per cent.; in spite of that help, of 170 factories by the end of 1914 only 43, and by the end of 1915 only 36, were working.

According to the U.S. Comm. Report, No. 303, 28th December 1915 (quoted in *J. Soc. Chem. Ind.*, 1916, p. 304), the Compañia de Salitres de Antofagasta was going to construct new works, producing about two million quintals nitrate per annum. Various plants of other companies are resuming operations, so that the nitrate produced will be able to supply any probable demand in the future. The exportation for 1916 will probably be about sixty million quintals. The Report of 16th March 1916 states the production of nitrate in Chili during 1915 = 38,147,000 quintals (of 46 kg. each), the export = 43,984,000 quintals.

According to *Chem. Ind.*, 1916, p. 248, seventy-five new nitre factories were erected in Chili in 1915; in January 1916 one hundred and sixteen factories were in full work. The total exportation of nitre from Chili in 1915 was 43,984,684 quintals, of which 21,168,997 quintals went to Great Britain and the European Continent, 1,703,130 to the Mediterranean, and 18,426,878 to the United States.

urge the following points:—

(1) The "refraction method" should be altogether abandoned. It yields very inaccurate results, and is indefensible from a chemical point of view.

(2) One of the following methods for the direct estimation of the nitric nitrogen, which yield correct results, should be employed: Lunge's nitrometer method; Schloesing-Grandeau's method, as improved by Wagner; Ulsch's method.

(3) In the case of Chili nitrate intended for agricultural purposes, the certificate of analysis should only state the percentage of nitrogen; the (incorrect) calculation for sodium nitrate is only to be allowed in exceptional cases, with all reserve.

(4) In the examination of Chili nitrates intended for technical purposes, besides the direct estimation of the nitrogen, also the impurities should be estimated, and the analysis should take account of any potassium compounds present.

Fresenius (*Rep. on the 5th Intern. Congr. f. angew. Chem.*, 1903) agrees to these demands. So does Beck (*Z. anal. Chem.*, 1906, p. 669), according to whom the refraction method may yield results 1·5 per cent. in excess of the truth. Stroof (*Chem. Ind.*, 1883, p. 369) found even an excess of 2 per cent.

In the refraction method any potassium nitrate present is altogether overlooked. This may amount to several per cent. even in refined sodium nitrate, and is of importance, because for the purposes for which sodium nitrate is used (*e.g.*, the manufacture of nitric acid and of explosives), the superiority of its nitrogen percentage over that of potassium nitrate plays

Devarda (*vide infra*, p. 62).

Complete Analysis of Nitrate of Soda, except the Estimation of Nitrate and of Perchlorate.

(a) *Moisture.*—Of a well-mixed finely ground sample 0·8000 g. is weighed off in a platinum crucible and cautiously heated over a very small flame, up to the point where the nitre is just fused. With good practice this point is very exactly reached without the aid of a thermometer. The crucible is allowed to cool in a desiccator, and weighed. It is then again heated to the same point as before, in order to observe the constancy of weight.

Or else 10 g. nitrate of soda is dried in an air-bath at 130° up to constancy of weight.

(b) *Insoluble Matters.*—Fifty g. nitrate of soda are exactly weighed in a beaker on a balance indicating at least 0·05 g. quite sharply. It is dissolved in water and filtered through a filter, tared by another filter of exactly equal weight. The washed residue is dried together with the tared filter, and weighed.

If the appearance of the residue on the filter indicates the presence of notable quantities of organic substances, the filter is burned together with the insoluble matter, to ascertain approximately the amount of organic substance. In this case the previous drying of the residue is best performed at a higher temperature, say 120° to 130°, because otherwise a slight difference would be found between the weight of the residue dried and that of the ignited residue.

(c) *Estimation of Chloride, Sulphide, Lime, Magnesia, and Soda.*—Five g. is dissolved on a filter, placed over a 500-c.c. flask, by pouring on boiling water. After washing, any sand present remains on the filter and calculated for NaCl. Another 50 c.c. is brought to boiling, and barium chloride is added; the precipitated barium sulphate is collected, weighed, and calculated as $CaSO_4$. For the estimation of lime and magnesia 20 g. nitrate is dissolved in 1000 c.c. water, and in 500 c.c. of this solution the lime is estimated by means of ammonium oxalate, the magnesia by ammonium phosphate. The soda is found, after estimating all the other constituents, either by difference or by adding to 100 c.c. of a solution of 20 g. nitre in 1000 c.c. water some sulphuric acid, evaporating to dryness, and igniting the residue up to constancy of weight. The weight of calcium and magnesium sulphate is deducted, and the remainder calculated for Na_2O. If potash is present, this is, of course, deducted as well.

(d) *Estimation of Potash.*—This was formerly done by converting the nitre into sulphates and "indirect analysis," which, however, for such small quantities of K_2O yields quite uncertain results. Far more accurate is the estimation of potash by several times evaporating the nitre with concentrated hydrochloric acid and precipitating the potash by platinum chloride, or by conversion into perchlorate (Caspari, *Z. angew. Chem.*, 1893, p. 68).

The potash is calculated as potassium nitrate, of which 100 parts are equivalent with 84·078 parts $NaNO_3$.

Estimation of the Nitric Nitrogen.

We cannot in this place enumerate all the various methods for the estimation of the nitrate, and refer for this purpose to Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. pp. 309 *et seq.* We here describe only the most important of these methods.

(a) *Method of Ulsch* (Beck, *Z. anal. Chem.*, 1906, p. 671)—

pipette by fusing the end off, partly filled with water, is put into the neck of the flask, and this cooler is kept from adhering too tightly by means of a platinum wire. When after ten minutes the reduction of the nitre acid to ammonia is accomplished, the liquid adhering to the cooler and platinum wire is washed off into the flask, 200 c.c. water and 20 c.c. caustic-soda solution (sp. gr. 1·35) are added, and the flask connected with an apparatus for distilling off the ammonia, consisting of a Liebig cooler and a tubulated receiver, connected with a Peligot tube, preferably of the shape shown in Fig. 3, in which the absorbing-liquid cannot be drawn back into the apparatus.

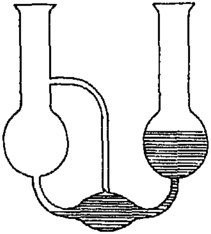


FIG. 3.

The connection between flask and cooler is made by an elbow-tube with a bulb at the end. (Since some alkali might be given off to the distillate from the glass, some chemists make the cooler of Jena glass.) The flask is placed on a wire net in a slanting position and heated by a strong flame, whereby all the ammonia is driven out within twenty-five to thirty minutes. The NH_3 is absorbed in 15 c.c. seminormal sulphuric acid, of which about 4 c.c. is diluted with water and placed in the Peligot tube, the other 11 c.c. is placed in the receiver. The liquid is retitrated with seminormal caustic-soda solution, methyl-orange serving as indicator. The contents of the receiver and the Peligot tube are washed out, diluted to 1000 c.c., and titrated by means of a burette, divided in ½ c.c. The purity of the reagents employed must be ascertained by a blind test, and a test for any ammonia present in the sample of nitre must be made. Each cubic centimetre of seminormal

Brandt (*Chem. Zeit.*, 1898, p. 22) points out that impurities

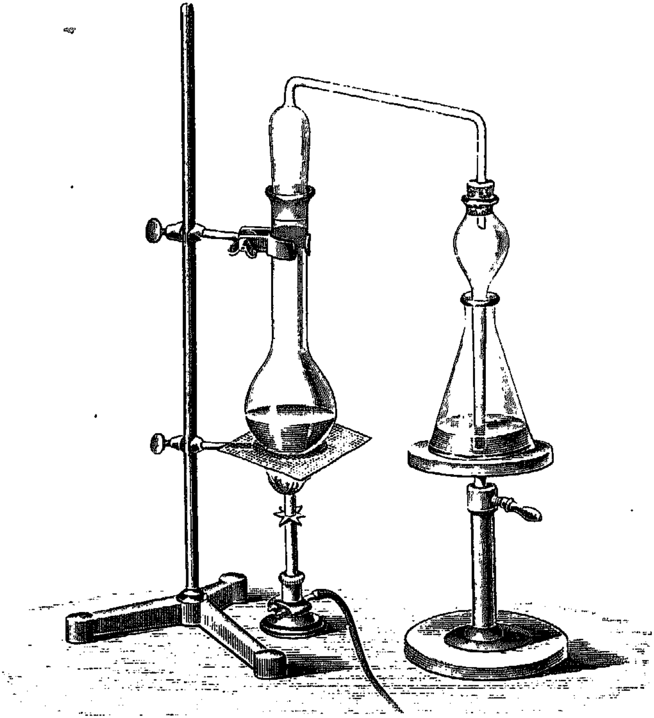


FIG. 4.

in the commercial ferr. hydr. reductum may cause errors up to 8 per cent.

Vogtherr (*Chem. Zeit.*, 1903, p. 988) recommends for us in the Ulsch method the apparatus shown in Fig. 4, originally intended for the determination of nitrogen by the Kjeldahl method, which allows of carrying on the digestion with sulphuric

Kleiber (*Chem. Zeit.*, 1909, p. 479) reduces the nitrate to ammonia by means of tin protochloride, iron filings, and water. He dissolves 10 g. of the nitre in 150 c.c. water. Of this solution he places 7·5 c.c. = 0·5 g. nitre in a flask holding 700 to 1000 c.c., adds 5 g. tin protochloride, 15 c.c. concentrated hydrochloric acid, and 4 to 5 g. iron filings, heats for ten to fifteen minutes on a water-bath or wire net by a small flame, adds 90 to 100 c.c. water, a small piece of paraffin, and 40 c.c. concentrated caustic-soda solution, and distils off the ammonia, using a strong flame from the commencement, so that the distillation is finished in half an hour. The receiver is charged with 20 c.c. seminormal sulphuric acid, allowing 0·1 c.c. of seminormal acid for any ammonia remaining in the distillation flask.

(b) *Method of Devarda* (*Z. anal. Chem.*, 1894, p. 113).—This excellent and much employed method is founded on the conversion of nitric acid into ammonia in an alkaline solution by the alloy of Devarda: 45 parts aluminium, 50 copper, 5 zinc (sold by the Aluminium-Industrie A. G., Neuhausen, Switzerland). This alloy is as brittle as glass, and easily powdered. Ten g. of the nitre is dissolved in 1000 c.c. water, and 50 c.c. of this solution (= 0·5 g. nitre) is placed in an Erlenmeyer flask holding 600 to 800 c.c., together with 60 c.c. water, 5 c.c. alcohol, and 50 c.c. caustic-potash solution of sp. gr. 1·3. Then 2 to 2·5 g. of the powdered Devarda alloy is added, and the flask at once connected with the distilling apparatus. The flask is slightly heated. After half an hour the reaction is finished, as shown by the slackening of the evolution of hydrogen. Heat is again applied and the distillation commenced; then the heat is increased, and the reaction finished, about half of the liquid having distilled into the improved Peligot receiver (Fig. 3). The NH_3 collected in seminormal sulphuric acid is estimated as described *suprà* in connection with the Ulsch method (p. 60).

0·15 per cent.

Treadwell and Wegelin (Wegelin's Inaugural Dissertation) employ the same method. Knecht (*J. Soc. Chem. Ind.*, 1915, p. 126) treats the nitre with caustic soda and titanium sulphate or chloride, which transforms the nitric nitrogen at once quantitatively into ammonia. He employs as much solution of the nitrate as corresponds to 0·1 g. KNO_3, treats this in a copper flask with an excess of caustic soda and 20 c.c. titanium sulphate or chloride, and removes the ammonia formed by distillation.

(c) *Lunge's nitrometric method* is described in our text, p. 132, and more explicitly on pp. 380 *et seq.*

It is founded on the reactions:

$$(1)\quad 2HNO_3 + 2Hg_2 + 4H_2SO_4 = 2Hg_2SO_4 + 4H_2O + 2SO_5NH$$

(nitrosulphonic acid).

$$(2)\quad 2SO_5NH + Hg_2 + H_2SO_4 = Hg_2SO_4 + 2SO_5NH_2$$

(sulphonitronic acid).

$$(3)\quad 2SO_5NH_2 = 2H_2SO_4 + 2NO.$$

The nitric oxide evolved and measured indicates the following quantities of nitrates:—

No.	$NaNO_3$.	KNO_3.	No.	$NaNO_3$.	KNO_3.
c.c.	Grammes.	Grammes.	c.c.	Grammes.	Grammes.
1	0·0037964	0·0045155	6	0·0227884	0·0270930
2	0·0075928	0·0090310	7	0·0265748	0·0316085
3	0·0113892	0·0135465	8	0·0303712	0·0361240
4	0·0151856	0·0180620	9	0·0341676	0·0406395
5	0·0189820	0·0225775			

The results agree within 0·2 per cent. when working with an ordinary nitrometer, or within 0·1 per cent. when employing a separate "agitating-vessel," as described in our text, p. 386, which also permits much more cleanliness in working.

a ground-glass joint. The stopcock is triple bored, and the nitric acid is measured by transference to a gas burette (*cf.* our text, p. 380). He also describes a reversible gas-measuring burette having a tap at each end, an enlargement at one end, and graduated through its entire length. If after absorption of one constituent of a gas mixture the remaining volume is so small that it is contained entirely within the enlarged bulb, the burette is reversed, and the volume can then be read off on the second reversed scale.

(d) *The method of Schloesing and Grandeau*, improved by Wagner, consists in reducing the nitrate by means of ferrous chloride to nitric oxide, and measuring the latter. It is principally used for estimating the nitrates in water; we refer to its description in Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. p. 317.

Ruff and Gersten (*Z. anorg. Chem.*, 1911, lxxi. p. 419) show that this method in the presence of arsenic trioxide or hydrogen sulphide yields too low results, through the formation of nitrous acid or of ammonia.

Bowman and Scott (*Chem. News*, cxiv. p. 39) titrate the nitrate by a solution of ferrous sulphate, standardised by potassium bichromate or nitrate, with addition of sulphuric acid.

(e) *Ignition with Chromates or with Quartz.*—The chromate method is described in Lunge-Keane's *Technical Methods*, i. p. 318. It consists in heating the substance with a mixture of acid and neutral potassium chromate; the loss of weight is $=N_2O_5$. Of course, no carbonates must be present.

In the same way as the chromates, acts powdered quartz, as shown by Reich (*Z. anal. Chem.*, 1862, i. p. 86).

Fresenius (*Z. anal. Chem. Ind.*, 1862, p. 184), Abesser (*ibid.*, 1873, p. 282), and Pauli (*J. Soc. Chem. Ind.*, 1897, p. 494)

Sodium perchlorate has been detected in all samples of commercial Chili nitre, and since it is injurious in many applications of this, it must always be taken into account. Many methods have been devised for its estimation, all of them based on its conversion into chloride, which is then determined, deducting the chloride originally present and estimated in another sample.

Sodium chlorate has also been found in many samples of Chili nitre.

The various methods for the estimation of perchlorate and chlorate are described in Lunge-Keane's *Technical Methods*, vol. i. pp. 319 *et seq.*

NITRIC ACID.

Page 133. *Properties of Nitric Acid.*—According to Baxter and Grover (*J. Amer. Chem. Soc.*, 1914, xxxvi. p. 1089), nitric acid, when concentrated by distilling through quartz tubes, contains no sensible quantity of dissolved impurities, and the acid distilled through well-seasoned pure platinum is equally pure, except minute traces of base metals dissolved. They insist upon this resistance of *pure* platinum to pure hot nitric acid, in opposition to Jannek and Meyer (*Z. anorg. Chem.*, 1913, lxxxiii. p. 71), who assert that nitric acid, if treated in platinum vessels, takes up traces of platinum.

Creighton and Githens (*J. Franklin Inst.*, 1915, pp. 161 and 703; *Chem. Trade J.*, 1915, p. 165) have determined the boiling-points and vapour tensions of nitric acids of various concentrations at various pressures; their results do not materially differ from those formerly published.

The viscosity of nitric acids of various strength has been determined by Boersfield (*J. Chem. Soc.*, cvii. p. 1907).

An investigation of the constitution of nitric acid by optical means has been made by Schaefer (*Z. anorg. Chem.*, 1916,

Specific gravity of Acid.	Temperature, ° C.			in 15 days. Grammes per square metre surface.
		In 15 days.	In 105 days.	
1·52	0	0·54	1·03	15
1·52	5	0·92	1·57	25
1·52	18	1·42	2·58	38
1·52	28	4·27	6·54	116
1·39	8	8·76	16·70	237
1·39	28	31·10	58·50	845
1·13	18	11·78	22·40	320
1·13	28	46·10	82·60	1250

In a second series of experiments the bottles were left open, exposed to the air; the corrosion was in this case considerably greater than in the first series, partly on account of absorption of moisture by the acid. The plates were most deeply corroded at the surface of the liquid. Attempts to protect the metal by coating it with celluloid varnish, cellulose acetate, caoutchouc, and paraffin were unsuccessful; but by heating it for about an hour at 400° to 500° C. its resistance to the attack by nitric acid was much increased, though this treatment cannot be recommended for thin aluminium vessels, as it impairs the mechanical strength of the metal. Welded aluminium was found to be as resistant to nitric acid as the untreated metal. The rate at which aluminium is attacked by nitric acid is increased by the presence of copper, sodium, or magnesium in the metal, or chlorine or hydrochloric acid in the acid. The author concludes that nitric acid can be safely transported in aluminium vessels, provided that the metal is of high purity and the acid is at its maximum concentration, but great care is necessary in using aluminium vessels for the preparation of nitrocellulose, as the rate at which they are attacked is much accelerated by hydration of the acid and rise of temperature.

Seligman and Williams (*J. Soc. Chem. Ind.* 1916 condition affecting the rate of dissolution is *temperature*. Over a considerable range of temperature an increase of 10° C. is sufficient to increase the rate of dissolution by 100 per cent. By attention to this factor the life of aluminium vessels used for the storage or transport of nitric acid can be greatly increased. Next to temperature, *concentration* plays the most prominent part in determining the rate of dissolution of aluminium in nitric acid. The most active solvents are mixtures containing between 20 and 40 per cent. by volume of nitric acid of 1·42 sp. gr., whilst on the other hand some acids made from the atmosphere, and containing 94·7 per cent. of HNO, were found to be almost without effect on aluminium. A sample of the metal suspended in this acid for seventy-one days lost only 0·0004 g., equivalent to a dissolution of 0·015 mg. of aluminium per 100 sq. cm. per twenty-four hours. The extreme inactivity of acid of this strength is held to account for the great success which has attended the use of aluminium transport vessels by the Norwegian makers of nitric acid. Concerning the effect of *impurities* of nitric acid, the presence of up to 0·05 per cent. of *chlorine* in the nitric acid was not found to affect the rate of attack of the latter upon aluminium. Similarly, no acceleration could be noted on the addition of 0·01 per cent. of *iodine*. On the other hand, the presence of a trace of *sulphuric acid* was found to promote the rate of attack, 0·04 per cent. being sufficient to raise the rate of dissolution by about 70 per cent. The rate of attack is increased by the presence of *the lower oxides of nitrogen*. If the acid is kept free from such lower oxides, the rate of attack on aluminium can be reduced considerably. The effect of the oxides of nitrogen produced by the interaction of nitric acid and aluminium in stimulating the attack is held to account for the fact often observed in practice, that dissolution is most rapid in crevices or corners and no "pitting" has been observed. The practical conclusion to be drawn from the authors' investigation is that aluminium can be used with great advantage for dealing with strong nitric acid, provided that the latter be cold and that the apparatus be suitably designed. For *hot* nitric acid of any concentration, aluminium can have but a very limited life. Dilute nitric acid, if cold, could in many cases be handled in aluminium with success, although the life of the aluminium will not be so long as where the metal is exposed only to the action of the strong acid. Owing to the higher rate of attack by dilute nitric acid, storage and transport tanks, after being emptied, should either be washed out thoroughly or so sealed that moisture cannot get in and so dilute the acid which remains in the tank. Finally, aluminium should only be used with great caution for handling mixed acids, and where aluminium covers and domes are used above vessels containing such mixtures, care should be taken to prevent splashing of the contents upon the aluminium.

In the Fr. P. 451812 of the Norsk Hydro-Elektrisk Kvaelstofaktieselskab it is stated that aluminium is not attacked by liquids containing not less than 65 per cent. of nitric acid and not more than 5 per cent. of nitrogen peroxide, and its use for apparatus dealing with acid liquids is claimed.

Manufacture of Nitric Acid.

Page 139. An enumeration of the patents for the manufacture, purification, and concentration of nitric acid is given by Oelker in *Z. f. d. ges. Schiess- und Sprengstoffwesen*, 1914, pp. 317 *et seq.*, and pp. 329 *et seq.*

Page 140. *Material for Nitric-acid Retorts.* — Instead of ordinary cast-iron, special compositions of metals have been place we mention only those which have found an extended and successful application for nitric-acid retorts, pumps, etc. These are:—

(a) *Tantiron*, a specially treated ferrosilicium, manufactured by The Lennox Foundry Co., Ltd., Glenville Grove, New Cross, London, S.E. (*vide* our text, p. 1129).

(b) *Ironac*, made by Houghton's Patent Metallic Packing Co., 10 St Mary-at-Hills, London, E.C.

Carnell (*Chem. Trade J.*, 1916, p. 182) states that *tantiron* contains from 14·00 to 15·00 per cent. silicon; 0·05 to 0·15 sulphur; 0·05 to 0·10 phosphorus; 2·00 to 2·50 manganese; 0·75 to 1·25 carbon (graphite). Its melting-point is about 1232°; sp. gr. 6·8; tensile strength 6 to 7 tons per superficial inch. *Duriron* contains 14·0 to 14·5 silicon; 0·25 to 0·35 manganese; 0·20 to 0·60 total carbon; 0·16 to 0·20 phosphorus; below 0·05 sulphur. Melting-point 1370° to 1400°; sp. gr. 7·00; textile strength 25 per cent. less than cast-iron.

Page 154. *Uebel's Apparatus for the Manufacture of Nitric Acid.*—The German patents for that process (taken out by the Chemische Fabrik Rhenania) are Nos. 106962 and 127647.

The style of working of the Uebel process has been improved by further patents. According to Uebel's B. P. 19881, 1913 (Ger. Ps. 261874 and 277092; Fr. P. 461452; U.S. P. 1141994), the whole of the sulphuric acid required for decomposing the nitrate is at first only mixed with part of the charge of nitrate in the still and heated to 140°, at which temperature the whole of the nitrate introduced is decomposed, yielding highly concentrated nitric acid (phase 1); then the remainder of the nitrate is introduced, and its complete decomposition effected by raising the heat to 160° to 170° (phase 2). In the first phase the nitrate and the sulphuric acid can be introduced at the same time and lead to frothing over, to explosive gas-developments, and to losses of nitric acid. The new process effects the production of highly concentrated nitric acid, a very even distillation, very hygienic work, free from danger, and an increase of production, as the stills have not to be allowed to cool down from one charge to the other.

Page 159. The Badische Anilin- und Sodafabrik has for the process described in the text obtained the French patent No. 406969.

The Chemische Produktenfabrik, Pommerensdorf, Stettin, and G. Schuler (Ger. P. 261634) make nitric acid in a retort with a cylindrical bottom, in which the mass is moved by a revolving screw from the cold to the hot end. There are partitions arranged so that the gases can be separately carried off from every compartment and condensed. At the lower end of the retort there is an overflow for the bisulphate.

Klages and the Saccharinfabrik A. G. vorm. Fahlberg, List & Co. (B. P. 3264, 1913; Ger. P. 267869; U.S. P. 1099452; Fr. P. 264561; Aust. P. 66307) produce nitric acid in a continuous manner by allowing potassium nitrate and sulphuric acid to run at the same time in approximately equivalent proportions on to the surface of a large mass of potassium bisulphate, kept fused in a retort. The freshly formed bisulphate is continuously removed by an overflow. The fused bisulphate occupies about a third of the retort space.

For the process mentioned in the text, p. 1553, de Jahn has obtained the Ger. P. 252374.

Chatfield (B. P. 16512, 1891) employs a large excess of sulphuric acid for decomposing the nitrate, in order to obtain a residue easily fusible at the temperature of reaction, which may be utilised for the production of hydrochloric acid, etc.

stoneware cooler, and runs off through a barometric tube 23 feet long. The liquid bisulphate passes at the other end of the pan again into a barometric tube 20 feet long, and issues in the open air. The B. Ps. are Nos. 3208 and 13842, 1914; U.S. P. No. 1130104.

Claessen (B. P. 6102, 1915; Ger. P. 287795) puts the nitre, with addition of a little sulphuric acid or nitre-cake, through a briquetting machine, in order to obtain cubes of about an inch diameter, which are worked in the nitric-acid retorts much more easily than powdered nitrate.

The Du Pont de Nemours Powder Co. (U.S. P. of Beers, Nos. 1240351 and 1149711) heats the now frequently employed large-sized nitric acid retorts by means of an oil-bath, whereby a high yield and economy of fuel are attained.

Page 163. *Condensation of Nitric Acid.*—Leblanc (Fr. P. 462712) passes the vapours through glass tubes, cooled inside by means of concentric pipes, and outside. Hough (B. P. 101307, 1916) also describes a tubular apparatus for that purpose.

Page 168. *Replacing the Stoneware Apparatus by other Materials.*—The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (Fr. P. 451812) employs for cooling, condensing, and carrying nitric acid, vessels made of aluminium. These can be employed for acid containing less than 65 per cent. HNO_3, and not above 5 per cent. nitrogen oxides (*vide suprà*, p. 68).

According to Gebrüder Borchers (*Chem. Zeit. Rep.*, 1913, p. 87), alloys of cobalt and nickel, containing upwards of 50 per cent. cobalt, by the addition of 4 per cent. silver, acquire the property of not being acted upon by nitric acid, even in the dilute state.

is an extensive illustrated report on this system, which is very favourably judged.

Page 173. *Valentiner's Process for the Manufacture of Nitric Acid in a Vacuum.*—The German patent for this process is No. 63207.

Page 178. Further patents of Valentiner for his nitric-acid process (together with Gontard) are:—B. P. 4254, 1907; Aust. P. 36792; Fr. P. 374902; U.S. P. 920224.

On the manufacture of nitric acid by the Valentiner process in Japan a report has been made by Inoué (*Chem. Zeit. Rep.*, 1914, p. 399), who prefers this process to that of Guttmann, both from the commercial and the hygienic point of view. He found that by this process, with a well-cooled retort, at a temperature of 150° in the beginning of the distillation, a smaller yield of nitric acid, but of high concentration (98·2 per cent.), and at 180° a concentration of 97·95 per cent. was obtained.

Volz obtained the U.S. P. 500785 for manufacturing nitric acid with the aid of a vacuum.

Page 184. *Behaviour of Nitric Oxide.*—Briner and Boubnoff (*Comptes rend.*, clvi. p. 228) examined the behaviour of nitric oxide at various pressures between 50 and 70 atmos., and at temperatures between −80° and +300°. A liquid is gradually separated whose quantity serves as measure for the velocity of the decomposition; its analysis proves that primarily two reactions are going on:

$$(1)\quad \tfrac{1}{2}NO = \tfrac{1}{2}N + \tfrac{1}{2}O.$$
$$(2)\quad NO = \tfrac{1}{2}N_2O + \tfrac{1}{2}O.$$

phase is observed.

Baudisch (*Z. angew. Chem.*, 1913, p. 612) found that nitric oxide in the presence of water containing a few pieces of yellow phosphorus, acting as a catalyser, in daylight is gradually converted into nitric acid and ammonia, but by the rays of a mercury-arc lamp into nitrous acid and ammonia. From nitrogen and oxygen, when exposed to the light of the radiating sun of Monte Rosa, as well as in that of the mercury-arc lamp, besides hydrogen peroxide and ozone, also nitrogen oxides are formed.

Page 184. *Behaviour of Nitrogen Trioxide and Nitrogen Tetroxide.*—According to H. A. and M. Baker (*Chem. News*, 1913, cvii. p. 5; *J. Chem. Soc.*, 1912, ci. p. 2339), a sample of nitrogen trioxide, kept during three years over phosphorus pentoxide, showed at atmospheric pressure a boiling-point of 43°, instead of $-2°$; it had, therefore, been transformed into an isomeric modification. Nitrogen tetroxide, which otherwise boils at 22°, after being most thoroughly dried, can be kept at 69° without boiling.

B. M. Jones (*Chem. Soc. Trans.*, 1914, cv. p. 2310) ascertained from the vapour pressures of nitrogen trioxide, which had been kept for two years over phosphorus pentoxide, that in the liquid state it consisted essentially of blue molecules of the formula N_4O_6, with a few molecules of NO_2 (or N_2O_4) and NO. On being evaporated, N_2O_6 dissolves (almost completely at 140°) into N_2O_3, and equal volumes of NO_2 and NO. On cooling, the inverse reaction takes place. In the gaseous state N_4O_6 and N_2O_3 are nearly or quite devoid of colour.

Egerton (*J. Chem. Soc.*, 1914, p. 647) discusses the vapour pressures of nitrogen tetroxide.

Raschig (*Z. anorg. Chem.*, 1913, lxxxiv. p. 115) writes on nitrogen hexoxide and nitrogen isotetroxide.

Lunge (*Z. angew. Chem.*, 1906, p. 907; 1907, p. 1716).

Klinger (*ibid.*, 1914, p. 7).

E. Müller (*Z. anorg. Chem.*, lxxvi. p. 230).

The application of nitrogen peroxide to the bleaching of flour is discussed by Scherings (*Chem. Weekblad*, xii. p. 46) and Steensma (*ibid.*).

Page 190. *Absorption of Nitrous Vapours.*[1]—Berl and Innes employ towers filled with tetraeders of wire-gauze. For the absorption of nitrous gases by water, in order to form dilute nitric acid, these tetraeders are to be made of aluminium wire; for the absorption by alkaline liquids, in order to produce nitrites, of iron wire.

The Dynamit-Aktiengesellschaft vorm. Nobel (Ger. P. 267874) absorbs dilute nitrous vapours by esters of aliphatic acids, *e.g.* amyl acetate. This substance at ordinary temperatures absorbs 20 per cent. of its weight of NO_2 and N_2O_3, whereas the organic absorbents formerly tried absorbed only from 1 to 1½ per cent. of the nitrogen oxides. The solution of these in amyl acetate easily gives off again the nitrogen oxides when it is heated and air is passed through. In the same way act butyl acetate, amyl valerianate, and amyl formate. From these solutions the dissolved nitrogen oxides can be also obtained by the direct action of water in the form of nitric acid of commercial concentration.

Bosch and Wild (U.S. P. 1115164) obtain technically pure nitrates from nitrogen oxides by adding definite quantities of steam to gaseous mixtures containing nitrogen oxides, and passing the mixtures over the oxides, hydroxides, or carbonates of the alkaline-earth metals at such temperatures (but not above 300°) that the water set free in the formation of nitrates remains in the state of steam.

much less absorbing power for those gases. The burning may be performed by the excess of heat of the gases intended for absorption; if these have a temperature of about 800°, this suffices for burning all the lime required for the absorption. The Fr. P. is 465740; the Norw. P. 26882. Their Ger. P. 287307 describes the application of fused calcium nitrate in the shape of drops.

Fenaroli (Ger. P. 283956) allows nitrogen oxides to act upon gaseous chlorine, given off from liquid chlorine. The nitrosyl chloride formed dissolves in the liquid chlorine. Such solutions *may be employed, e.g., for* bleaching *flour.*

Häusser (B. P. 7419, 1914; Fr. P. 469649; Ger. P. appl. H59140) absorbs dilute nitrous gases gradually by water with application of long oxidising spaces, interposed between the absorbing-apparatus. He has experimentally found that the absorption of nitrous gases by water takes place very rapidly, if the nitric oxide, always formed over again by the equation

$$3HNO_2 = HNO_3 + 2NO + H_2O,$$

finds opportunities of reoxidation. The more frequent changes there are between absorption and oxidation, the smaller the absorbing-apparatus may be kept, and the expensive stoneware apparatus of the present process can be almost entirely done away with. According to his Dutch P. 1417, of 1916, a number of small absorption-cells are arranged in a column, through which the washing-liquid passes continuously.

Page 190. *Further Processes for the Treatment of Nitrogen Oxides.*—Lelarge (Ger. P. 253078), Oetling (Ger. P. 253156), Moest and von Berneck (U.S. P. 1049754), Kirchhofer (Ger. P. 262464).

Page 191. *Concentration of Nitric Acid.*—Collett's patents nitric-acid vapours are carried through several towers in which sulphuric acid is run down; that acid is cooled between each two towers. The evaporation of the nitric acid is carried out in several communicating vessels, and the vapours are passed into a dephlegmating-apparatus at various heights; from this apparatus continuously acid containing 15 to 20 per cent. HNO_3 is run off.

Page 194, line 17. For the process mentioned here, the Société anon. le Nitrogène has obtained the Fr. P. 424598.

Pauling's English patents have been mentioned on p. 193 of our text. He has also obtained U.S. Ps. 993868, 1031864, 1031865, 1074287, 1079541; Aust. Ps. 48815, 48816; Fr. P. 450448, 463859. The newest forms of his system are described in Ger. Ps. 257809 and 274165. According to these, it is best to employ nitric acid as free as possible from organic substances, nitrogen oxides, and nitrosulphuric acid. From a mixture of 1 part of 48 per cent. nitric acid and 2 parts of 94 per cent. sulphuric acid it is easy to obtain nitric acid of 96 to 98 per cent., without any weaker acid coming behind. It is best to charge the mixture on the top of a vertical tube, filled with the dividing bodies, and to introduce from below dried, but not superheated steam, or inert gas containing very much aqueous vapour. According to his Fr. P. 463859 (transferred to the Norsk Hydro-Elektrisk Kvaelstofaktieselskab), nitric acid of 30 per cent. is gradually passed through a series of evaporators, whereby acids of 40, 50, 60, 68 per cent. are obtained. The vapours are passed through dephlegmators, from which the acid goes back to the evaporators. The vapours are introduced into the dephlegmators at various heights; the acid to be concentrated also goes into a dephlegmator, a little below the entrance of acid of 15 to 20 per cent.

55242; U.S. P. 1050160 (taken out by Moest and Berneck). They obtain concentrated nitric acid by treating nitric acid of 60 to 62 per cent. with liquid or gaseous nitrogen peroxide, and then with oxygen, on the counter-current system. The oxygen enters at one end of the apparatus, the N_2O_4 at an intermediate point. Preferably it is obtained by passing a current of oxygen through liquid N_2O_4. The oxygen is employed in slight excess; according to their Ger. P. 249329, they employ oxygen in the compressed state, and reintroduce any oxygen and nitric oxide gases, escaping at the bottom, into the system.

A new patent of that firm (B. P. 4345 of 1915, taken out by O. Imray; U.S. P. 1180061, and Swed. P. 40600, of Moest) states that if nitric acid is intimately mixed with a larger proportion of liquid nitrogen peroxide than corresponds to the maximum of solubility, two separate layers are formed, both of them consisting of nitric acid and NO_2, but one of them—mostly that of lower specific gravity—contains a more concentrated acid, up to 100 per cent. The other layer contains a more diluted acid than that which has been at first used. Thus it is possible to obtain highly concentrated nitric acid by means of liquid NO_2. The NO_2 is eliminated by distillation from the layer containing the more concentrated acid. The other layer, containing dilute nitric acid and NO_2, may be enriched, for instance, by treating it with oxygen, and further concentrated by the new process. In order to avoid loss of NO_2, a reflux apparatus is employed. The process may be operated under pressure; it is advantageous to agitate well.

Sohlmann and Lundholm (U.S. P. 1009197) concentrate nitric acid (made from atmospheric nitrogen) by hot gases, which are used in succession for concentrating dilute sulphuric acid, distilling strong nitric acid from its mixture with sulphuric acid, and ultimately for the concentration of dilute nitric acid way they cool down and allow most of the nitric acid to separate in a concentrated form. The non-condensed remainder of nitric acid is retained in the second tower and by other suitable apparatus. His Austrian patent is No. 38937. A plant for carrying out this process has been erected by the Aluminium-Industrie Akt. Ges. at Chippy, near Siders (Valais).

According to Fr. P. 472775 of the Farbwerke Höchst, and U.S. P. 1145162 (taken out by Moest and Eckardt), nitric acid is concentrated in a retort, provided with a dephlegmating column, heated to a suitable temperature by means of a coating or by the nitric vapours themselves. The acid to be concentrated is continuously run into the column, and the strong acid continuously run out at the bottom.

Raschig (B. P. 3208, 1915; Ger. P. 286973; U.S. Ps. 1130104, 1163174) combines two apparatus for the concentration of nitric acid, both of them consisting of shallow, flat-bottomed pans, made of cast-iron, lined with lead, with ribs compelling the liquid to travel a long way. In the first of these pans vapours of concentrated nitric acid are evolved from dilute nitric acid of 50 per cent. and strong sulphuric acid (92 per cent.), the mixture being heated to about 150° by means of steam of 10 to 12 atmospheres' pressure, circulating in a worm cast in the pan-bottom. On its way through the pan nearly all the nitric acid is evaporated; it is condensed in a stoneware worm, cooled outside, and runs off as highly concentrated nitric acid. The dilute sulphuric acid coming out of this pan is forced by air-pressure into a second pan, placed 20 ft. above the first, working under a vacuum, and likewise heated to 150° by indirect steam. In this pan the dilute sulphuric acid gives off water and the remainder of the nitric acid in the state of vapour. Both of them are condensed in a stoneware worm, the highly diluted nitric acid running off freely by a descending pipe, 33 ft. long, and a dipping-pot. This dilute nitric acid is packing for absorbing and reaction towers.

Rossi (Fr. P. 455531) brings nitric acid into contact with hot air, with or without steam, in such a manner that the temperature of the gases on leaving the apparatus is below 100°. According to his Fr. P. 455532, a mixture of dilute nitric acid with one and a half times its weight of concentrated sulphuric acid is passed on in the contrary direction to a current of air and steam, by which process very pure nitric acid, up to 99·8 per cent., is obtained. According to his Fr. P. 463830, nitric acid is concentrated up to 42° Bé. in a vacuum apparatus, allowing of dephlegmation and fractionation.

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. Ps. 27239, 1913; 19792, 1914; Ger. Ps. 278367 and 289745; Fr. Ps. 465504 and 474995) pass the vapours of dilute nitric acid through a tower fed with concentrated sulphuric acid, from which practically dry vapours of nitric acid escape. Part of the sulphuric acid is run out of the tower at the bottom, cooled, and reintroduced higher up. The dilute sulphuric acid formed is before its reconcentration passed through an apparatus in which the nitric acid contained in it is driven out by a current of air; the vapours are passed through the first tower. According to their Ger. P. 292385 the liquid is evaporated by indirect heating. The central part of the tower is kept at the low temperature required for the drying operation, by drawing off part of the running-down acid cooling it, and re-introducing it into the tower at a higher point.

Titlestad (U.S. P. 1178888) makes a mixture of vaporised and liquid nitric acid meet a counter-current of concentrated sulphuric acid.

Schall and the Stickstoffwerke Akt. Ges. at Herringen (Ger. P. 280965) pass a mixture of dilute nitric acid and a drying-agent through a tower, provided with a central tube through which heating-gases flow, and which on the outside nitroglycerin.

Baxter and Grover (*Chem. Zeit. Rep.*, 1915, p. 229) found that *platinum* resists the action of *pure* nitric acid. On evaporating such acid in platinum dishes, no residue was formed.

Page 194. *Manufacture of Nitric Monohydrate* (nitric acid of 100 per cent).—The Verein chemischer Fabriken at Mannheim (B. P. 20189, 1912; Ger. P. 281211; Fr. P. 462290; U.S. P. 1115192, taken out by Hausmann) employs for this purpose a still of the form of a flat dish, heated merely at the bottom, the top being cooled by air or cold gases. Thereby any vapours of sulphuric acid are kept back, and the nitric acid is obtained free from sulphuric acid. The depth of liquid in the still is only 20 to 30 mm., and the liquid is compelled by concentric partitions to flow in a long course over the heated bottom, so that the mixed acids can be continuously run in and the sulphuric acid can be continuously run out. The nitric acid vapours are carried away by air passing over the liquid, and are condensed in worms, tourills, and towers, which is much more easily done than in vacuum apparatus. This apparatus, when comparing the total heating surfaces, does five or six times the work of a vacuum plant; besides most highly concentrated and monohydrated nitric acid, it produces only slight quantities of weaker acid, quite free from nitrogen peroxide.

Hof (Ger. P. 279131; U.S. P. 1099368) employs for the continuous distillation and concentration of acids an inclined tube, made of quartz glass, zirconium glass, or other acid-proof materials.

The Salpetersäure-Industrie Gesellschaft, Gelsenkirchen, has, besides the patents mentioned in the text on p. 195, obtained with platinum anodes, employing a current density of 200 amperes per superficial metre, and 7 volts. The oxidation is completed in 17000 ampere hours.

Nitrogen pentoxide is obtained by Russ and Pokorny (*Monatshefte f. Chem.*, 1913, p. 1051; *Chem. Zentr.*, 1913, ii. 1271) in one operation by the fractional distillation of a mixture of concentrated nitric acid and phosphorus pentoxide in a current of ozonised oxygen. The ozone prevents the decomposition of the N_2O_5 into oxygen and lower nitrogen oxides. In order to remove the last traces of water, the vapours are before their condensation passed through a long layer of phosphorus pentoxide. The nitrogen pentoxide is almost completely condensed at a temperature of −80°. Its vapour pressure is at 34° equal to the atmospheric pressure, whilst it is still in the solid state. An exact determination of the fusing- and boiling-points is impossible, since a dissociation sets in; the statements on those points in the chemical treatises are erroneous.

Page 195. *Compound of Nitric and Sulphuric Anhydride.*—Schultze and the General Chemical Co., New York (U.S. P. 1047576), prepare a solid compound of the approximate formula:

$$N_2O_5(SO_3)_4H_2O,$$

in various ways, *e.g.*, by heating SO_3, or the gaseous mixture obtained by contact processes, in nitric acid of at least 94 per cent. In a cylindrical lead vessel a mixture of about 300 parts fuming oil of vitriol, containing 60 per cent. free SO_3, and 70 parts nitric acid of 96 per cent. HNO_3 is treated with the vapours of SO_3 and HNO_3, while heating the lower is gradually introduced into cooled nitric acid (96 per cent. HNO_3). The compound thus obtained does not fume in the air; it is crystalline and hygroscopic, sp. gr. 2·18. It fuses between 93° and 104°; at 170° it is partially decomposed, with effervescence, and gives off nitrous vapours. These properties allow of easily packing and cheaply carrying it. Owing to its uniform composition that compound can be advantageously employed in lieu of the ordinary liquid nitrating mixtures.

Page 195. *Preparation of Pure Nitrogen from Air or Fuel Gases.*—Willson and Haff (U.S. P. 1084774) burn sulphur with a limited quantity of air, pass the mixture of nitrogen, oxygen, and sulphur dioxide thus formed through milk of lime, and the nitrogen (together with traces of oxygen) over heated sulphur, absorbing the SO_2 formed as above.

Meves (Ger. P. 179782) obtains pure nitrogen by liquefying air, *e.g.*, by the Linde process, and fractional distillation of the liquid air.

Neumann (Ger. P. 281518) repeatedly compresses air up to the liquefaction of oxygen, pure nitrogen remaining in the gaseous state. An apparatus for this purpose is described by Taubert (Ger. P. 277717).

Weilnböck (Ger. P. 193410) absorbs the oxygen by moist, fresh bark.

Frank and Caro (Ger. Ps. 183702 and 204882) pass fuel gases over a metal containing its oxide, whereby the carbon monoxide and the hydrocarbons are burnt to carbon dioxide, which is removed by absorption.

Similar to this are the methods of Hurford (U.S. P. 914279) of the Nitrogen-Gesellschaft, Berlin (Ger. P. 215608; Fr. P. 468349), of E. A. and J. Behrens (Ger. P. 226942).

is by means of a dividing-plate squirted upon the top of the lower column, over which part of it descends, whilst another part goes into a worm, fixed at the top of the upper column and connected with a vacuum pump. The evaporation of the air at reduced pressure under appropriate conditions causes its cooling down to the boiling-point of nitrogen.

Siemens and Halske (Ger. P. 286514) obtain chemically pure nitrogen by heating the nitrogen compounds of alkali metals with tantalium powder.

The Nitrogen Company at Ossining (Ger. P. 260804) obtains nitrogen from atmospheric air (and hydrogen from water or steam) by fixing the oxygen by metals easily reduced by coal, *e.g.* lead or tin. The metallic oxides thus obtained are taken up by a liquid agent and conducted to a place where they are reduced to metals for further use. The "liquid agent" employed consists of the alkaline chlorides or carbonates, or other salts fusing below 800°. The operation is performed by a large crucible, heated in a furnace, within which a smaller crucible is placed bottom upwards, for collecting the gas. The heating may be effected in any suitable way, also by an electric alternating current.

Wallace and Wassener (B. P. 3147, 1912) pass air over phosphorus, and separate the products in a complicated way.

The Industriegas-Gesellschaft für Sauerstoff- und Stickstoffanlagen (Ger. P. appl. J13634) describes an apparatus for separating the constituents of atmospheric air by liquefaction, brought about by compression, counter-current cooling, and expansion, and separation by partial revaporisation. The liquefied gas is collected in a vessel, reaching from the pressure-reducing valve to the oxygen collector, through which passes later on.

Page 195. *Preparation of Pure Nitrogen Protoxide.*—Torley and Matter (Ger. P. 276069) prepare N_2O by continuously introducing ammonium nitrate in the solid form or in solution into a vessel containing a fused mixture of salts, *e.g.*, sodium nitrate, potassium nitrate, and ammonium sulphate.

Preparation of Nitric Oxide.—The Norsk Hydro-Elektrisk Kvaelstof Co. (U.S. P. 1111301) prepare NO by employing round the reaction zone of an electric arc an atmosphere rich in oxygen, and round this one of atmospheric air.

Page 195. *Manufacture of Pure Nitrogen Peroxide.*—The Badische Anilin- und Sodafabrik (Ger. P. 231805) remove any NO_2 present in nitrogen oxide, free from oxygen, or gaseous mixtures containing it, dry the NO, and convert it by dry oxygen into NO_2 (N_2O_4).

According to their Ger. P. 242288, nitrogen peroxide is obtained from gases containing small quantities of it in a solid form by the cooling produced by compressing the gaseous mixture, removing the heat of compression, and allowing it to expand adiabatically. For separating N_2O_4 in the liquid form a temperature of -80° is sufficient.

Raschig (*Z. angew. Chem.*, 1907, p. 102) obtained an isomeric nitrogen tetroxide which he calls "isonitrogen tetroxide," in the shape of blue crystals, by the action of air on nitric oxide at low temperatures.

Badermann (*Zsch. f. d. ges. Schiess- und Sprengst.*, 1914, p. 326) describes cylindrical railway trucks for carrying liquid nitrogen peroxide, on the foundation of a report made by the Chemische Versuchsanstalt at Berlin. Nitric peroxide is manufactured at Bodio on the Gotthard line, and sent out in cake by itself, because on the large scale this is impossible without fusing it, which destroys every known description of apparatus. Nor can this be prevented by mixing the nitre-cake with silica, silicates, anhydrous sulphates of sodium, potassium, calcium, etc., as proposed by Benker (*vide* p. 1449). But it is possible by heating the nitre-cake with coal, as prescribed in the Ger. P. 63189 of Rommenhöller and Luhmann, or with sawdust (B. P. 6898, 1904; *vide suprà*, p. 196). According to the new process (Ger. P. 263120) a carbonisable substance, like sawdust, peat, etc., is put into the liquid hot bisulphate as it is run out of the nitric-acid still; this causes a tempestuous evolution of gas, and the bisulphate solidifies as a loose, spongy, extremely porous mass. On calcining this in a muffle, the coal formed thereby acts as a reducing agent and goes away as CO_2, whilst the bisulphate turns even more porous and therefore less fusible, and can therefore be calcined at the normal temperature of a saltcake furnace. For this purpose from 2 to 10 per cent. sawdust is stirred into the hot bisulphate run out of the nitric-acid stills, and the mixture is allowed to solidify on a cooling place, forming a black, spongy mass which on calcination is converted into a white mass without fusion, and forms neutral sulphate of normal composition.

Löffler (U.S. P. 1104911) describes the same process.

Stanes and Rogé (B. P. of Hunnybun, No. 18605, 1914) heat the acid sulphate with sulphur in a muffle, collect the liberated sulphur dioxide, and convert the residual anhydrous sulphite into bisulphite by treatment with sulphuric acid.

Mackenzie (B. P. 13907, 1915; Ger. P. 291775) melts nitre-cake in a saltcake-pot; after driving off the moisture and the weak acid, the charge is pushed on to the roaster, where the sulphuric acid is driven out and led into a Glover tower or other suitable apparatus.

Haas (*Chem. Zeit.*, 1916, p. 571) uses nitre-cake as a partial lava, or similar matters, or of cast iron with an insulating layer for keeping it hot. The fire gases enter at one end, perpendicularly to the bath, and leave the apparatus at the other end. The flame should be clear, and not smoky. The nitre-cake is introduced mechanically and continuously by an opening lined with "neutral iron"; the neutral sulphate is removed at the opposite end by several outlets at different heights. In order to protect the cast-iron trough against the destructive action of the liquid bisulphate, and the liquid neutral sulphate against contamination by the iron of the trough, flues are provided underneath the trough, through which cooling-air is blown. By this means, and by a suitable depth of the trough, it is possible to produce between the fused mass and the trough a pasty layer.

Other ways of dealing with nitre-cake are described in the twelfth chapter, pp. 1488 *et seq.*

A committee of users of sulphuric acid in the West Riding of Yorkshire, together with some Government officials, report on nitre-cake as a substitute for sulphuric acid (*Chem. Trade J.*, 1916, p. 28; *J. Soc. Chem. Ind.*, 1916, p. 109). From experiments made in a number of mills it appears that nitre-cake can be used in place of sulphuric acid in the textile industries for the extraction of grease from wool, etc., and for other purposes, dissolved in hot water and used hot. The chief difficulty is the cost of railway carriage and cartage; proposals are made for overcoming this by establishing depots at certain centres.

The use of nitre-cake in the textile industries was discussed in the Manchester Chemical Club on 27th October 1916 (*Chem. Trade J.*, lix. p. 393).

According to Klemm (*Chem. Ind.*, 1915, p. 311), sodium bisulphate can be employed in sizing paper as a partial formerly employed proportion of sulphate of ammonia, and a quarter of an hour afterwards nitre-cake to the amount of 20 per cent. of the formerly used aluminium sulphate, in the form of a cold solution of 20 to 25 g. per litre.

According to *J. Soc. Chem. Ind.*, 1915, p. 857, a committee of the Chemical Society and of the Society of Chemical Industry has been formed for the purpose of studying a better utilisation of nitre-cake. Proposals for this purpose were to be directed to the address of the secretary, Mr Ch. G. Cresswell, Broadway Chambers, Westminster, London, S.W. In response to this a number of suggestions were made, a digest of which is given in the same *Journal*, 1915, p. 1121, and which are briefly summarised here. Heating the nitre-cake with common salt, thus obtaining hydrochloric acid and saltcake. Heating with magnesite, in order to make Epsom salts. Using it to replace sulphuric acid in the manufacture of superphosphates. Roasting it with iron scale, in order to get off the available acid. Using it in the making and glazing of slag bricks. Sprinkling it on manure heaps, in order to fix ammonia. Heating it with mixed sulphide ores, in order to extract the zinc. Removing the free acid by blowing steam or air into the fused mass. Extracting copper from copper pyrites. Using it to decompose soapsuds. Using it for making blancfixe and sodium hydrosulphite. Heating it with leather clippings, whereby much of the nitrogen is converted into ammonium sulphate. Roasting it with felspar, and obtaining potash alum. Using it, mixed with salt, for roasting copper, zinc, and nickel ores. Using it for converting sodium chromate into bichromate. Opening up wolfram ores. Treating it in a saltcake furnace for recovering sulphuric acid and sodium sulphate. Neutralising the free acid, and reducing the sulphate by means of fine coal to sulphide. Utilising the potash contained in it in the manufacture of superphosphate.

facture of Sulphate of Ammonia.—The Sulphate of Ammonia Association (*Chem. News*, 1916, vol. cxiii. p. 175; *J. Gas Lighting*, 1916, p. 74) point out that the recommendation of using nitre-cake as a substitute for sulphuric acid in the manufacture of sulphate of ammonia has met with somewhat severe criticism. This proposal involves the reduction of the amount of ammonia in the sulphate to 24 per cent., and possibly less, and can be, therefore, only advocated as a temporary expedient during the war. The presence of free nitric acid in nitre-cake causes damage to the leadwork of the saturator, and ultimately destruction of ammonia; the maximum percentage of nitric acid in the nitre-cake used by sulphate-of-ammonia makers should be 0·05 per cent. The Association recommends confining the use of nitre-cake to 10 per cent. of the acid. This amount should be dissolved in water until the solution shows 100° Tw. at 200° F.; or dissolved in mother-liquor from the saturator. The best working strength is 80° to 84° Tw.; 1 vol. of this solution should be used with every 10 vols. of 70 per cent. sulphuric acid, and it will yield a salt containing from 23 to 24 per cent. of ammonia.

If large quantities of nitre-cake are used, sulphate of soda is precipitated in the saturator, and an irregular quality of salt is obtained, containing down to 15 per cent. ammonia. The working of the bath is irregular, owing to the impossibility of control without frequent titration. The salt produced often contains 2 per cent. acid after leaving the centrifugal machine, and in this case moisture is absorbed during the storage, and it is not possible to pack the products in bags. When less than 10 per cent. of nitre-cake by weight of the acid is used, these difficulties are partially overcome. *Vide* also *Chem. Trade J.*, 1916, lix. p. 548.

Page 108. *Utilisation of Waste Acids from Nitrating*

1913, pp. 217-230) which contains nothing essentially new. The steam used for this purpose is to be superheated, which can be done in lead apparatus up to 250° to 230°, or, preferably, in cast-iron apparatus up to 400°. Thus nitric acid of 38° to 40° Bé. is obtained. The remaining sulphuric acid contains still 2·5 up to 3 per cent. nitrosulphonic acid; it can be sufficiently denitrated by evaporating it in porcelain dishes or the like to 66° Bé.

Other processes for this object are described in our text, pp. 168, 1179, 1555.

Page 199. *Recovery of the Nitric Acid from the Washing-liquor in the Manufacture of Nitrocellulose.*—Claessen (B. P. 6363, 1915; Ger. P. 288459) points to the fact that the amount of acid lost with the washing-liquor may be about two or three times as great as that required for the production of nitrocellulose. Heretofore it has been proposed to recover the nitric and sulphuric acids by distillation; also to subject successive portions of the pyroxylin to rinsings with the same water, and to neutralise the water between the successive rinsings, until it is sufficiently charged with nitrate to be advantageously recovered. By the present process most of the nitric acid contained in the washing-liquor is concentrated to such an extent as will make its recovery a paying operation. This is effected by repeated use of the same washing-liquor until the desired degree of acid concentration is obtained, whereupon the nitric acid contained in the liquor is converted by reducing agents, such as ferrous sulphate and sulphuric acid, into nitric oxide, which is converted into nitric acid in a manner similar to that employed in the production of nitric acid from the air. The reaction products, such as the ferric-oxide salts, are again converted by means of reducing agents, such as iron, to protoxide salts for re-use in the process. The well-known fact that nitric acid is split up by heating below its boiling-point, and completely so in the presence of sulphuric acid, which takes up the water formed in the reaction, forming nitroso-sulphuric acid:

$$HNO_3 + H_2SO_4 = HNSO_5 + H_2O + O.$$

This action goes on, until the sulphuric acid has taken up nearly 40 per cent. water. The nitroso-sulphuric acid forms with water: sulphuric acid and nitrogen trioxide, thus:

$$2HNSO_5 + H_2O = 2H_2SO_4 + N_2O_3.$$

The latter in contact with air and water forms nitric acid:

$$N_2O_3 + O_2 + H_2O = 2HNO_3.$$

Traine and Hellmers, Wever and Brandenburg (Ger. P. 269656), prepare nitric acid by heating calcium nitrate, treating the evolved gases with moist oxygen or moist air, and adding before or during the introduction of fresh calcium nitrate into the heating apparatus a sufficient quantity of indifferent, difficultly fusing material, in order to cause the fluxing mass not to come into direct contact with the hot walls of the apparatus, but to be enclosed and absorbed by the newly added material, which prevents or at least lessens the caking up of the fluxed calcium nitrate and its adhesion to the sides of the apparatus.

W. Mills (U.S. P. 755378) dissolves substances containing lead in hydrofluosilicic acid, treats the solution with an alkaline or earthy-alkaline nitrate, and decomposes the plumbic nitrate formed thereby by sulphuric acid.

Baynes and the Chemical and Electrolytic Syndicate, of London (B. P. 7273, of 1895; U.S. P. 632394), prepare nitric acid continuously by heating a mixture of alkaline nitrate with ferric oxide in a thin layer, in a retort into which air or a mixture of air and steam is introduced.

previous operation. A barium or strontium compound may be added, in order to convert the silica into an insoluble silico-aluminate.

According to their Ger. P. appl. S42495, to the mixture of nitrate and alumina 10 per cent. calcium carbonate is added, in order to keep the mass in a porous state, and the mixture is moulded into briquettes, which are treated as above.

Nodon (Ger. P. 274346) obtains nitric acid immediately from the natural saltpetre earths, *e.g.* peat, by electrolysis. He places in the nitre-bearing soil porous vessels containing dilute nitric acid and coke, which serve as an anode. The nitric acid obtained by the electrolysis of the nitrate contained in the soil collects in these vessels; the alkalies or alkaline earths, formed by the electrolysis, migrate to the cathodes, which consist of cast-iron or sheet-iron plates sunk in the nitre pits. The Joule heat developed by the current is utilised for keeping up an even temperature favourable for the reaction. According to one of the patent claims, the peat soil is kept alkaline by placing lime or calcium carbonate between the anodes and the soil. The floor of the peat moor has an electric resistance of about 3 ohms per cubic metre. The electric current has about 10 volts; it produces at the anode nitric acid, at the cathode lime. Many details on the process are given in the patent description. The process is described at length by Dary in *Chem. Trade J.*, 1914, vol. liv. pp. 75 *et seq.*

The Oesterreichische Verein für chemische und metallurgische Produktion at Aussig (Ger. P. 280967) prepares nitric acid by heating ammonium nitrate with so much sulphuric acid that it suffices at least for producing ammonium hydrosulphate. This allows of driving off the nitric acid completely at temperatures not much above 120°, and is finished up to 152°. If less sulphuric acid is employed, losses are caused by the necessity of working at higher temperatures, whereby the

Manufacture of Sulphuric Acid and Alkali, 1911, vol. III. pp. 318 *et seq.*

Page 204. *Nitric Acid from Atmospheric Nitrogen.*—Bender (Ger. P. 258935; U.S. P. 1011014) attains the continuous production of the oxides of nitrogen, or of nitrogen and sulphur, from gas mixtures containing nitrogen, oxygen, and sulphur compounds, by employing fuel forming large quantities of water in burning. The admission of air and the velocity of the gaseous current are regulated in such a way that the combustion gases contain an excess of 7 to 10 per cent. oxygen and 11 to 14 per cent. CO_2. Hydrocarbons, hydrogen, mixed gases, etc., are burned, by passing definite quantities of air into the gas-producer above the fuel; the gases produced are cooled, and the water is removed before they leave the producer. Only then the NO is oxidised into N_2O_4, which is transformed into nitric acid or nitrates. Any sulphur present in the fuel is completely transformed into SO_2.

The Westdeutsche Thomasphosphatwerke (B. P. 5010, 1914; Ger. Ps. 157629 and 182297) heat a mixture of air with steam or detonating-gas up to the commencement of the dissociation of H_2O, and remove the hydrogen formed before cooling by diffusion. The oxygen formed combines in the nascent state with nitrogen, forming NO_2, which is not dissociated at higher temperatures. The hydrogen diffuses through the white-hot porcelain tubes employed, whilst the coarser molecules of H_2O, NO_2, O_2, and N_2 travel along and escape at the end of the tubes.

The B. P. of the Société l'Air Liquide for their process mentioned in the text, p. 206, is No. 18475 of 1910.

Lymn (B. P. 3194, 1913) passes the mixture of N and O over fireclay, highly heated by gaseous fuel, with or without steam.

of a shaft-like, hermetically closed gas-producer. By the combustion of the fuel in the furnace the water in its porous walls is vaporised and passes through the walls over to the combustion gases. If the outgoing gases are in their hottest zone suddenly well cooled, a large yield of nitrogen compounds is obtained, such as nitric acid, ammonium nitrite, ammonium nitrate, etc. This sudden cooling can be, for instance, produced by a hollow grate, cooled by water or air. At a temperature of 2000° in the furnace about 1 vol. per cent. NO and 0·25 vol. per cent. NH_3 are formed. Bender's U.S. P. 1172863 is for the same process; it mentions aluminium oxide as the nitrogen carrier. The French patent is No. 474107.

Meigs (U.S. P. 1120960) manufactures nitric and sulphuric acid at the same time, by burning sulphur or sulphur ores with air in a mechanical furnace in such manner that principally SO_2 and N are formed, and transforms the gases through a catalyser into SO_3 and NH_3; the latter is then oxidised into nitric acid.

The Bremen-Besigheimer Oelfabriken (B. P. 4023, 1914) produce a catalyser, consisting of a mixture of metals or metallic oxides and carbon, by calcining organic metal compounds or a mixture of metal compounds with carbon, etc., up to the point where the product has become pyrophorous.

Herman (Ger. P. 281084) burns methane in air, enriched with oxygen, under high pressure in a space connected with a cooler for the combustion gases in such a way that no condensed water can get back into the reaction space, working either directly with excess of oxygen and formation of a flame, or indirectly with flameless surface combustion within a zirconium mass. Yields of 3 to 4 vols. per cent. have been obtained, if the conditions were rightly observed. For the formation of 1 kg. HNO_3 (100 per cent.) at most 2·5 cb.m. of methane *i.e.* 22000 calories are required. According to his not react with water at ordinary temperatures, but on heating with fused alkali it yields ammonia, and with oxidising agents nitric acid.

Classen (U.S. P. 1178440) brings a mixture of nitrogen oxides, oxygen, and ozone, containing less than 74 per cent. oxygen, into contact with an oxidising catalyser containing nickel. The nitrogen pentoxide produced by the reaction is absorbed by an aqueous alkaline solution.

The Société le Nitrogène (Fr. P. 453099) improves catalytic masses, consisting of copper and cupric oxide mixed with clay, by the addition of aluminium oxide, which increases their porosity and keeps them much longer in an active state.

Hlavati (Fr. P. 453207; Ger. Ps. 277054, 275343) employs for the combination of N with O and H a series of chambers filled with mixtures of the metals of the platinum group with titanium, in proportion of their atomic weights, precipitated on asbestos. Here the gases ionised by electric discharges, possessing a temperature of 1000°, are cooled down, first to 450°, then to 200°, and so forth. Instead of the expensive ionising process, the catalysation may be activated by uranium ore, monazite, etc.

Krauss and Staehelin (B. P. 26499 of 1913; Ger. P. of 26th July 1913; Fr. P. 465045) prepare compounds of N and O at high temperatures and various pressures by burning liquid or gaseous fuel in a mixture of N and O. The combustion is effected in a flameless way within highly refractory porous or granular materials, *e.g.*, oxides of chromium, titanium, uranium.

The Badische Anilin- und Sodafabrik (B. P. 12977, 1913; 13848, 1914; 7651, 13291, and 13297, 1915; U.S. P. 1173532; Ger. P. 275518) employ ruthenium and its compounds for promoting oxidising reactions which with other oxygen carriers, also those of the platinum group, cannot be brought about at all, or only with great difficulty; also in the form of or entirely replaced by lead.

According to their Ger. P. 275343, the contact substance is prepared by soaking the porous carrier with solutions of titanium and platinum salts, which are afterwards reduced by hydrogen or ammonia.

Sinding-Larsen and Storm (Swed. P. 36205) oxidise atmospheric nitrogen by the chlorine or sulphur compounds of lithium or titanium at high temperatures.

Frank and Finke (U.S. P. 1101424; Fr. P. 439244) prepare fertilisers by passing air over copper heated to 800° to 900° in a gas-tight chamber, and bringing the nitrogen left behind into contact with a mixture of 6 parts of lime + 10 silicium, or 8 lime, 3 silicium, 2 iron, kept at 1000° to 1050°. The nitrides thus obtained are free from dust, non-poisonous and non-hygroscopic, and can be directly employed for fertilising purposes.

Dobbelstein (*Glückauf*, 1912, p. 289; *Chem. Zeit. Rep.*, 1913, p. 206) describes the production of nitric acid by the explosion of coke-oven gases with atmospheric air in shells, holding 100 litres, at an initial pressure of 1·95 atmos., which rises to 14 atmos., lasting one and a half seconds, while the temperature gets up to 135°.

Esnault-Pelterie (B. P. 1275, 1916) compresses the mixture of N and O suddenly, so as to produce a very high temperature, and then immediately expands it so as to produce cooling and prevent dissociation of the nitrogen oxides obtained, for which purpose he describes a suitable apparatus.

Prytz (Dan. P. 21232, 1916) places a mixture of N and O in a vessel under a pressure of above 50 atmos. and heats it therein.

Häuser (*Z. Verein. deutsch. Ingen.*, 1912, p. 1157) investigated the combustion of nitrogen by oxidising gas mixtures with gas conduit leading to the first contact space has branches capable of being shut off, leading to the single heat-exchangers, so that the gas temperatures of each compartment can be regulated by the exchange of heat between the inflowing and outflowing gases.

Ditz and Kanhäuser (*J. prakt. Chem.* [2], lxxxviii. p. 456; *Chem. Zentr.*, 1913, p. 2009) discuss the formation of nitrate and nitrite in calcium hydrate, exposed to the action of air.

Wilhelmi (Ger. P. 270062) describes an apparatus, heated by fire gases, for exposing gases to the action of contact materials, in which for the purpose of easy mounting and dismounting, charging, etc., an annular contact space and a removable cover are placed on the annular fire space.

Eggert (*Z. Elektrochem.*, 1914, xx. p. 370; 1915, xxi. p. 349) discusses the activation of hydrogen and oxygen by platinum on the basis of an extended experimental investigation.

Leland L. Summers gives a lengthy description of the various processes for the utilisation of atmospheric nitrogen in *Proc. Amer. Inst. Elect. Eng.*, March 1915.

Lachmann (Ger. P. 289844) in the production of nitrogen oxides from N and O keeps the heating and reaction products separate. For example, a gaseous mixture containing free N and free O is passed over an auxiliary substance (such as magnesia) which has been previously heated to a high temperature by direct contact with combustion gases (produced preferably with gas rich in oxygen, instead of with air). During the production and utilisation of the heating gas, the temperature may be controlled by circulating part of hot waste combustion gases near the furnace walls. The furnace described is divided by radial walls into contiguous units.

Bedford, Sleaford, and Erdmann (U.S. P. 1200696) describe the preparation of light voluminous ferric oxide, suitable for

According to him, the present demand for nitrogen compounds in the whole world is 750,000 tons per annum; it increases yearly by about one-twentieth, and is covered by nitre and ammonium sulphate. (We pass over Haber's utterances concerning nitrogenous fertilisers, provision for procuring the ammonia, etc., as in this volume we treat only of nitre and nitric acid.) The stock of nitre existing in the Chilian beds will last about another fifty years, assuming an annual increase of consumption by 50,000 tons. When treating of its replacement by the oxidation of atmospheric nitrogen with the help of electricity, it is sufficient to take account of the consumption of energy for the reaction, $N + O = NO$; for the nitric oxide thereby produced passes over by itself into nitric acid by the action of air and water. The formation of NO from N and O consumes 21,000 g.-cals. per molecule. If it were possible to obtain nitric oxide from air by employing the equivalent electric energy, it would be possible to fix 500 g. nitrogen per kilowatt-hour, and thereby quite easily to cover the world's requirements of nitrogen compounds. This, however, is a Utopian calculation, for no form of electric discharge is known by which, apart from the consumption of energy for the chemical action, no further electrical energy were consumed by transformation into heat. Even then the calculation shows a favourable result for the high-tension arc. If this has a temperature of 3500°, and the transformation were quantitative, a kilowatt-hour would still theoretically fix 113 g. nitrogen per hour; but practically only from 11 to 16 g. is attained, and the concentration of the nitrous gases does not exceed 2·5 per cent., in lieu of 42 per cent. to be expected by calculation. This necessitates large and expensive installations, and the employment of the cheapest and largest water-powers; and this directs the production of nitre from air into countries in which otherwise energy than for the combination of N and O is required for the combination of N and H; therefore the synthesis of ammonia has greater prospects of practical exploitation. (Just in that direction Haber has attained splendid results, which for the above-named reason we cannot discuss in this place.)

Russ (*Chem. Zentr.*, 1913, i. 216; *Chem. Ind.*, 1913, p. 534) contends that the assumption of a merely thermic formation of nitrogen oxides in the electric flame-arc cannot be kept up after the investigations of Haber and König; that formation must be ascribed to electronic shocks. By means of cold, silent discharges, ozone and nitrogen oxides are formed at the same time. An important part is played by the formation of "active" nitrogen, discovered by Strutt, who has described that modification of nitrogen, formed by the electric discharge, in a series of papers, partly with the cooperation of Fowler (*Roy. Soc. Proc.*, 1911, p. 219; 1912, A, pp. 56, 105, 262, 539; B, pp. 179, 302).

Tausent (*Z. Elektrochem.*, 1912, p. 314) showed that for the same duty vertical arcs are more favourable than arcs between horizontal electrodes, both with respect of stability and of the yield of nitric acid.

Strong (*Amer. Chem. J.*, 1913, l. p. 204) investigated the formation of nitrogen oxides by crown-shaped electric discharges, produced by passive electrodes, which deviate in their properties from the ordinary electric flame-arc. This kind of discharge does not allow of recognising in which zone the formation of ozone and that of nitrogen takes place. About the same amount of nitric oxide is formed by the positive and the negative corona. The consumption of energy in these experiments was 300 watts; that is, the same as with other flame-arc processes.

chemists on the ground of further experiments (*ibid.*, p. 603). Koenig and Elöd (*ibid.*, p. 2998) answer to this, and conclude that the chemical action of the gas entering behind the arc is always founded on the fact that part of it, owing to the violent movement in the discharge space, can always enter into this, so that the arc now acts upon a new gas mixture. If any mixture in the arc space is avoided, the additional gas acts merely as a diluent.

Tiede and Domcke (*ibid.*, 1913, p. 4095) again investigated the question of "active" nitrogen, and came to the conclusion that the yellow after-glow observed by Strutt and by Koenig and Elöd, which they attribute to the return of the nitrogen molecules, activated by electric discharges, into ordinary molecules of nitrogen, is not a property of pure nitrogen, but is owing to a certain content of oxygen; therefore that after-glow is not a proof of the existence of "active" nitrogen, but an extremely sensitive reagent for traces of oxygen mixed with the nitrogen. This explanation is entirely accepted by Franz Fischer (*ibid.*, p. 4103).

Saposhnikow, Gudima, and Kutuwoi (*J. Russ. Phys. Chem. Ges.*, 1913, p. 1076; *Chem. Zentr.*, 1913, ii. 1550; *Am. Chem. Soc. Abstr.*, 1913, p. 3923) examined the influence of the velocity of the blowing-through of air, that of the moisture, and that of the material of the electrodes upon the yield of nitric acid in the oxidation of nitrogen by the electric arc. The yield of nitric acid per kilowatt-hour first rises to a maximum of 65·3 g., afterwards goes down, and again rises to 1·90 of the proportion, V : Kw.

Baker, Tiede, Strutt, and Domcke (*Ber.*, 1914, p. 2283) made common experiments for clearing up the contradictions, mentioned above, between the results of Tiede and Domcke on one side, and those of Baker and Strutt on the other side; they found that, in fact, the addition of an immeasurably small

1914, p. 420); Koenig and Elöd (*ibid.*, pp. 516 and 523); Baker and Strutt (*ibid.*, pp. 801 and 1049); Kowalski (*Comptes rend.*, 1914, p. 625); Jevons (*Roy. Soc. Proc.*, 1915, p. 120); Strutt (*ibid.*, 1915, p. 303; 1916, p. 438; and *Chem. News*, 1916, p. 260); Koenig (*Z. Elektrochem.*, 1915, pp. 268-286); Tiede (Ber., 1916, p. 1741).

Hene (*Z. Elektrochem.*, 1914, p. 745) found that a higher yield of nitrogen oxides is obtained, if the oxygen is activated by sparks (whereby O_2 is partly transformed into O_3), than if the nitrogen is treated in the same way.

Lowry (*Phil. Mag.* [6], xxviii. p. 412) describes an oxidisable modification of nitrogen, obtained by electric sparking through air which is oxidised into nitrogen peroxide by ozone. This modification is unstable, and after a few seconds passes over into a form which is not oxidised either by oxygen or by ozone. He believes this modification to be the product formed in the first instance in the technical fixation of nitrogen.

Gorbow and Mitkewitch (*J. Russ. Phys. Chem. Ges.*, 1913, p. 1109; *Am. Chem. Soc. Abstr.*, 1913, ii. p. 950) find by theoretical speculations and practical experiments that the relation between the nitric oxide c, formed by the combustion of air under the influence of the voltaic arc, the volume of air d introduced into the furnace per hour and per kilowatt, and the number of grammes nitric acid, G, into which the nitric oxide can be transformed, is expressed by the formula:

$$8G/225 = cd \qquad (1).$$

From this it follows, first, that on changing at a given supply of air the conditions of combustion in such manner that there is always a certain definite percentage of NO kept up, the ideal duty is expressed by the hyperbolic formula:

$$c = b/(d+a) \qquad (\text{II}).$$

If instead of b/a, the letter b^1 is chosen, we obtain:

$$G = 225a(b^1 - c)/8 \qquad (\text{III})$$

and

$$G = 225bd/8(d+a) \qquad (\text{IV}).$$

For every given furnace there is not one definite equation of the type III, but quite a number of them, corresponding to the variation in the exploitation of the electric energy. The values of a (II) and b (II), a (III) and b (IV), etc., show a constantly varying value.

Technical Processes for the Manufacture of Nitrogen Oxides and Nitric Acid from Nitrogen by means of the Electric Current.

Russ and Ehrlich (B. P. 10992, 1912; Fr. P. 443620; Ger. P. 266345) submit a mixture of nitrogen and oxygen to the electric discharge in the presence of oxygen, whereby the lower nitrogen oxides, as they are formed, are converted into nitrogen pentoxide. The work is carried on until nearly all ozone is used up, whereby a maximum of N_2O_5 is formed; or else the gaseous current passing through the discharge chamber is increased in such a way that after the absorption of the N_2O_5 a gas rich in ozone is obtained. A high concentration of ozone is reached, if the N_2O_5 is taken out of the gas from time to time, or continuously, and if high temperatures are employed. They employ a glass Siemens tube, in which the electrodes are 4 mm. distant from each other, and a discharging chamber holding 140 c.c. The tube is cooled on the outside by water of ordinary temperature. The discharges are produced by a continuously interrupted current constantly decreases and the concentration of the ozone increases. On the other hand, the reduction of the velocity of the gas current below the above indicated limit leads to the decomposition of the nitric pentoxide. By this process it is possible to produce either nitric pentoxide as such, or to convert it into pure nitric acid or nitrates. The concentration of the ozone may also be increased by taking care to remove the N_2O_5 from the sphere of the reaction.

Their investigations on the electric oxidation of nitrogen are continued in *Wiener Akadem. Monatshefte*, 1915, pp. 317 *et seq.*

Naville, C. E. Guye, and P. A. Guye have obtained for the process mentioned on p. 221 of our text, the U.S. Ps. 1035581 and 1035723.

Their process is reported to be practically successful.

Vender's process (our text, p. 223), according to *Chem. Trade J.*, 1913, liii. p. 155, has been successfully worked out in a small experimental factory in Hungary.

Kaiser has obtained for his process, mentioned in our text, p. 225, further patents: Ger. P. 271517; Fr. P. 435967; Aust. P. 52284.

Bunet, Badin, and the Compagnie d'Alais have obtained for their process mentioned on p. 227 the U.S. P. 1035684. (The first name is in the text erroneously spelt "Brunet.")

Richert von Koch (B. P. 14528, 1911; U.S. Ps. 1051120, 1065144, 1055331; Ger. Ps. 249946, 260134, 261102, 262920, 265166, 276841; Austr. P. 65957) passes the pre-heated gases through an electric furnace, surrounded by a zone of less highly heated gases, in order to protect the electrodes, at a pressure essentially below that of the atmosphere. He describes a number of furnaces adapted to this purpose.

Wassmer (U.S. P. 985083; Ger. P. 262830) describes an electric furnace for the production of a light arc which exert one of the electrodes is shaped in such a way that it produces an annular stratum of the gases to be treated; the other, revolving, electrode is placed in the plane of the injected gases and forms an annular flame, the central plane of which coincides with the exit plane of the gases. By this means the gases are compelled to travel first through the hottest part of the flame and then through the outer zones, whereby a rapid oxidation and fixation of the oxides formed is brought about. Another furnace on this principle is described in his U.S. P. 1179927.

Rossi (Fr. Ps. 455530, 463821, 555530; B. P. 23959, 1913; Swiss P. 67428) oxidises atmospheric nitrogen by the action of electric light-arcs, formed between electrodes made of aluminium, zinc, or other metals sending out ultraviolet rays or electrones. The walls of the apparatus are coated with zinc.

Andriessen (U.S. P. 1058653) produces nitrogen oxides by forming a high-tension arc-flame, blowing air against this in the centre so that the arc is deformed and raised above the normal height, and exposing it to the action of unilaterally directed magnetic lines of force in a right angle to the deformation, so that it is lengthened and spread in disk shape over a large area over which the gases to be treated are conducted.

The German patents of Andriessen and Scheidemantel are Nos. 284341 and 285111; the Swiss P. 62344.

Du Pont (*cf.* our text, p. 226) has obtained for his process B. P. 17038, 1912; Ger. P. 279309; Fr. P. 446269; U.S. P. 1147150.

The Société générale des Nitrures (B. P. 22586, 1914; Fr. P. 474365) employs a mixture of carbon, bauxite or other forms of alumina, and iron which in the state of fine powder is exposed to the air; it gets heated and absorbs nitrogen from the air. Their B. P. 4387 of 1915 prescribes the use of contact substance ought to be in the most finely possible state of division.

E. K. Scott (*J. Soc. Chem. Ind.*, 1915, p. 113) gives illustrated descriptions of the apparatus of Birkeland and Eyde, Schönherr, Badische Anilin- und Sodafabrik, and Pauling (all of them described in our text), as well as of his own apparatus, for which he claims that they produce electricity more cheaply than the other systems, that they increase the production by 20 per cent. through employing in lieu of air a mixture of equal parts of N and O, and that they increase the yield by raising the working temperature by means of a three-phase alternating current from 3200° to 4200°, which brings up the theoretical yield from 819 up to 1850 kg. per kw.-year.

Fujiyama (B. P. 9259, 1914; U.S. P. 1090391) employs a closed chamber, containing a revolving drum, leaving a space between itself and the walls which contains electric heating apparatus. He describes an arrangement for charging the materials on to the drum and for discharging it in a cooled state; also an arrangement for conducting nitrogen through this discharging arrangement through the drum, to meet the materials.

Wielogalsky (Norw. P. 24195) concentrates the solutions of nitrates obtained from air in such a way that the ammonia is recovered as usual in an absorbing-apparatus, and the acid is partly or entirely converted by bases into nitrate. The nitrate solution is employed for taking up new acid, until it is sufficiently saturated.

H. D. Rankin (U.S. P. 1150786, assigned to the Rankin Process Co.; Fr. P. 479492) brings compressed air into contact with a flame produced by electric discharges in a vessel provided with a head or disk which is simultaneously reciprocated and rotated. Relatively stationary points on the disk are connected by electric conductors to a high-tension induction atmospheric air by liquefaction and rectification.

Page 214. *Further Investigations and Patents concerning the Oxidation of Nitrogen by means of Electricity.*

Morden (*Trans. Amer. Electrochem. Soc.*, 1908, p. 113; *J. Soc. Chem. Ind.*, 1909, p. 520).

Beckman (*Electr. Review, Chicago*, lix., pp. 533 and 598).

Kilburn Scott (*ibid.*, lxvii., pp. 887 and 896).

Neuberger (*Z. angew. Chem.*, 1905, p. 184).

Cramp and Hoyle (*J. Soc. Chem. Ind.*, 1905, p. 95).

Thonesen and Tharaldsen (U.S. P. 996951).

Weber and Schreiber (U.S. P. 981727).

A. Müller (*Z. angew. Chem.*, lxxvii. p. 324).

Lowry (*Trans. Faraday Soc.*, ix. p. 189; *Proc. Roy. Soc.*, 1911, p. 219; *Proc. Chem. Soc.*, 1912, p. 64).

Russ (*Z. angew. Chem.*, 1912, p. 586).

Russ and Ehrlich (Ger. P. 233031).

Bonnevie (U.S. P. 1173699).

Bucher (U.S. P. 1174667, 1174668, 1174944, assigned to the Nitrogen Products Co., Providence, R.I.).

Moody and Tucker (U.S. P. 1175007).

Scott and Howles (B. P. 3953, 1915).

Prim (Ger. P. appl. P20722, not Ger. P. 20722, as erroneously quoted in the text).

Zeitschrift für Elektrochemie, 1907, pp. 77, 190, 210, 225, 237, 280 (with numerous illustrations).

Krebs (Ger. P. 250684).

Grohmann (Ger. P. 250968; U.S. P. 1035873; B. P. 919 of 1912).

Phillips (U.S. P. 1035732).

Schönherr and Hessberger (U.S. Ps. 1032782, 1038208, and 1115340).

Fr. P. 259740).

Donath und Frenzel, Ueber die Ausnutzung des atmosphärischen Stickstoffs, Leipzig, 1907.

Albihn (Ger. P. 228755).

Ellis (U.S. Ps. 1002249 and 1007683).

Schönherr and Neuberger (U.S. P. 1003299).

Dary (*Electrician*, xlvi. p. 553; *Abstr. Amer. Chem. Soc.*, 1914, p. 1238).

Wolcott (U.S. P. 1116661).

Salpetersäure-Industrie A. G. (Ger. Ps. 258385, 269238).

Hoofnagle (B. P. 20950, 1912; U.S. Ps. 1051810, 1062772, 1169824).

Kochmann (U.S. P. 1055331; Ger. Ps. 260134 and 263652).

Hill and Bulteel (Ger. P. 245492).

Scheitlin (Fr. P. 451515).

Lee (Ger. P. 267003; U.S. P. 1051131).

Dynamit-Aktiengesellschaft vorm. Nobel (Ger. P. 267874; Aust. P. 55906).

Moscicki (Ger. Ps. 236882, 252271, 256295, 265834; U.S. P. 1097870; Aust. P. 65945).

Schnabel (Ger. P. 250270).

Zenneck and Vollmer (U.S. P. 1063760).

Helfenstein (Ger. P. 262325).

Hayden (U.S. P. 1066772, transferred to the General Electric Co.).

E. K. Scott (B. Ps. 14871 and 16014, 1912; 4723 and 4724 of 1913; Fr. P. 459660; U.S. P. 1113376). Also *Iron Age*, 1916, xcviii. p. 305.

The British Thomson-Houston Co. (B. P. 26082, 1912).

Siebert (U.S. Ps. 1033126, 1061786, 1073823, 1073870).

Harker and Scott (B. P. 866, 1913).

Aluminium-Industrie Akt. Ges. (Fr. P. 465807; Swiss P. 60532).

Adams (*Abstr. Amer. Chem. Soc.*, 1915, p. 1274).

Edwin, Hähnle, and Strasser (U.S. P. 1111301).

Summers (U.S. Ps. 113940 and 1130941).

Foss (Ger. P. 279641; U.S. P. 1200334).

Wilmowsky (B. Ps. 4723, 4724, 4725, 6136, all of 1913).

L. Hechenbleickner, assignor to the Southern Elektrochemical Co., New York (U.S. P. 1173960).

Page 221. P. F. Frankland (*J. Soc. Chem. Ind.*, 1915, p. 310) states that at Notodden water-power to the amount of 300,000 h.p. is to be utilised for the production of calcium nitrate, of which 150,000 tons, of 15 to 20 per cent. N, are to be obtained.

C. A. H. de Sacelles (U.S. P. 1183172) roasts blende (with the addition of C near the end of the roasting) with a regulated supply of air, so as to prevent the temperature of the charge from exceeding 1000°. This effects the decomposition and reduction of any sulphates, without volatilising any of the metal.

Page 227. *Process of Pauling* (Salpetersäure-Industrie Gesellschaft, Gelsenkirchen).

Additional patents:—

B. Ps. 22320 and 22322, 1910.

Ger. Ps. 241882, 244840, 246712, 250968, 257809, 258385, 259815, 268410, 269238, 274165.

U.S. Ps. 887266, 1031864, 1031865, 1074287.

Austr. Ps. 48815, 48816.

French Ps. 420803, 420804, 425765, 430111, 430112, 461326.

Swiss Ps. 53244, 56245.

The German patents 244840 and 246712 of the Salpeter-transformed from the divergent direction into a direction converging perpendicularly to the furnace axis, and ultimately parallel with it. Annular slits serve for separately taking out the gases of various concentrations.

Their Ger. P. 258385 describes water-cooled horn-electrodes for carrying out endothermic gas reactions, in which the central part, which is most exposed to burning out, is usable on several sides, by turning, after the wearing out of one plane, another plane against the flame. The electrodes consist of three parts, the upper and lower part being very little, but the central, movable part being very much, acted upon by the flame.

According to *Chem. Zeit.*, 1915, p. 40, the Pauling process, employing the horn-shaped light-arcs, is working at Patsch, near Innsbruck; at La Roche de Rame, near Briançon in France; at Legnano in Italy; and at Charlotte, N.C., where the Southern Electrochemical Company produces "nitric acid made from air" in a chemical pure state, containing 64 to 94 per cent. HNO_3.

Page 236. *Process of Birkeland and Eyde* (*Notodden Process, Norgesalpeter*).

According to F. C. Perkins (*Chem. Eng.*, xviii. p. 238), the furnaces at Notodden and Rjukan are working with a duty of 1000 to 3000 kw. The Notodden factory was employing 65,000 h.p.; that at Rjukan, 250,000 h.p.

According to *Chem. Ind.*, 1914, p. 221, the Société Norvègienne de l'Azote had greatly extended its production in 1913. The manufacture of "Norgesalpeter" at the works of Svägfos and Notodden employed about 55,000 h.p., and that at the Rjukan works 120,000 h.p., corresponding to a production of from

Ind. Eng. Chem., 1912, pp. 771 *et seq.*) we quote the following statements. The furnaces have a coating of cast steel and wrought iron, and are lined with firebricks, by which the air supplied to the flame is preheated. The nitrous vapours formed in the flame escape through a fireproof flue leading along the furnace shell. Every furnace is fitted with an induction spiral for regulating the force, whereby a quiet flame is produced, and the furnaces can go on for weeks without further regulation. Only once every three or four weeks the most exposed parts, viz., parts of the electrodes, must be renewed; the fireproof brickwork only every third or fourth month. The temperature of the flame is over 3000°, that of the exit gases is between 800° and 1000°. The central part of the furnace is shaped as a circular chamber, into which the electrodes are radially introduced, the air being blown in from below by a centrifugal fan-blast. The furnaces at Notodden consume from 1000 to 3000 kw., those at Rjukan altogether 3000 h.p. The cooling and further treatment of the gases is performed as above described. The Notodden factory now works with about 60,000 h.p., supplied by the two cataracts Lienfos and Gvaelgfos. In November 1911 the factories at Notodden, Gvaelgfos, Lienfos, and Rjukan altogether employed 200,000 h.p., 143 officers, and 1340 workmen.

In 1913 there were employed at Rjukan, 400 engineers and officers, and upwards of 2000 workmen. Of the "Norgesalpeter" thus produced, many thousands of tons are sent out as far as California and Hawaii, as fertilisers for fruit gardens and sugar plantations; the demand in 1913 was twice as large as in the year before. The product contains about 75 to 80 per cent. calcium nitrate, with 13·5 per cent. nitrogen.

According to W. O. Hermann (*Chem. Zeit.*, 1913, p. 918), during the next few years 250,000 h.p. per annum will be capital of about sixty millions Norwegian kroner (= £3,300,000). Apart from "Norgesalpeter," they will also take up the manufacture of pure nitrate of potash. The product primarily obtained, viz., nitric acid of 30 per cent., can also be brought up to very pure acid with 98 per cent. HNO_3, and not above 0·01 per cent. nitrous acid.

Apart from the patents concerning this process, enumerated on p. 238, a U.S. P. 1001018 has been obtained; also Norw. P. 24423 (*Chem. Zeit.*, 1914, p. 499), and Fr. P. 465470.

Communications on the production of nitric acid, nitrate of ammonia, and calcium carbide by the Nitrogen Products and Cyanamide Co., are made in *Chem. Trade J.*, 1915, p. 45, and by E. K. Scott, in *J. Soc. Chem. Ind.*, 1915, p. 113. At Rjukan, in South Norway, most of the nitric acid produced is, as before, neutralised by lime, and the solution of calcium nitrate is evaporated. On further heating, the mass fuses; according to Ger. P. 268828, it is stirred on cooling until a sufficient quantity of small crystals is obtained; the paste formed is passed on to a revolving iron drum, cooled inside, from which the crusts forming outside break off in thin layers, which do not cake together and which are easily reduced to powder. The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (B. P. 468 of 1913) effects the reduction of calcium nitrate to powder by running it in the fused state on to a perforated disk, placed in a shaft in such manner that the drops formed solidify before getting to the bottom of the shaft, which is promoted by introducing cold air, previously deprived of moisture by cooling. The powdered nitrate is removed as soon as it reaches the bottom of the shaft. The Fr. P. is No. 442514.

The cataracts near Aura are to be utilised for the manufacture of nitre to the extent of 200,000 tons.

According to P. F. Frankland (*J. Soc. Chem. Ind.*, 1915 for norgesalpeter, in metrical tons, were :—

	1912.	1913.	1914 (Jan. to Oct.).
Production	...	70,000	65,332
Exportation . . .	51,701	70,171	...
Consumption in Norway .	5,000	5,000	...

The figures given in *Chem. Zeit.*, 1914, p. 1000, for Norway are (tons):—

	Production.	Inland Consumption.	Importations of Chili Nitrate.
1905	127	5	707
1908	15,000	470	1,615
1910	18,500	1,850	258
1913	73,214	5.500	106

The new Birkeland furnaces consume 3000 kw. The percentage of nitric oxide in the exit-gases is now smaller than before, since the velocity of the air-current has been raised.

At the Rjukan factory, besides the Birkeland-Eyde furnaces, a number of Schönherr furnaces (p. 239) is working, to the extent of 1000 h.p.

Flusin (quoted in *Chem. Ind.*, 1914, p. 525) makes the following partly incomprehensible statements on the synthetical production of nitre at Notodden. Cost of electrical power, 156 frs. per electrical kilowatt, or 28·60 frs. per kilowatt-year. Chemical expenses, 167·50 frs. per kilowatt. Cost of production per ton of nitric acid, from 55 to 70 frs.; with a production of 500 kw. nitric acid per kilowatt-year, 128 to 152 frs. per ton of calcium nitrate, 218 to 250 frs. per ton of nitric acid; with a production of 500 kg. nitric acid per kilowatt-year, 107 to 126 frs. per ton calcium nitrate, 187 to

	Per cent.
$Ca(NO_3)_2$	76·15
$Ca(NO_2)_2$	0·05
CaO	0·15
MgO	0·30
$CaCO_3$	0·55
$MgCO_3$	0·35
Fe_2O_3	0·10
Al_2O_3	0·40
Insoluble	0·50
H_2O	21·45
	100·00

Page 246. *Further Patents of the Badische Anilin- und Sodafabrik for the Production of Nitric Acid, etc., from Air.*—(*a*) For the production of light-arcs and their use for oxidising nitrogen, Ger. Ps. 232926, 233729, 233967, 237562, 237796, 238367, 238368, 238958, 255732, 265413; B. Ps. 22715, 1909, and 13097, 1910; U.S. Ps. 1095425, 1095426, 1095427, 1095429. (*b*) For the treatment of gases produced, Ger. Ps. 229780, 231805, 242288.

According to the Ger. P. 265413 of the Badische, oxygen and nitrogen are combined by introducing into the zone of reaction a gas mixture rich in O and N, or pure oxygen, and outside of it atmospheric air. They employ a long, stable light-arc, burning in a tube, into which the reacting gases are introduced in the longitudinal direction, and the outer gases are carried along the outside of the tube in the state of vortex.

According to *Chem. Trade J.*, 1915, p. 575, a factory is being erected at the lignite works at Golpa-Tessinitz, near Bitterfeld, for producing nitric acid from atmospheric nitrogen by the process of the Badische, which is to work ultimately with 1000 million kilowatt-hours, and to cover the whole

(*Z. angew. Chem.*, 1908, pp. 2161 and 2209); Grau und Russ (*Chem. Zentr.*, 1907, i. p. 1172); Bodenstein (*Z. angew. Chem.*, 1909, p. 1154). For this purpose it is convenient to employ concentrated sulphuric acid as absorbent. The gases are first passed through a large bottle for the purpose of mixing and oxidation, in which they must remain at least one minute to get the oxidation as completely as possible up to nitrogen peroxide, and are then conducted through two intensely acting absorbing apparatus charged with measured quantities of concentrated sulphuric acid. For this purpose the bell-shaped washing-bottles, described by Wislicenus in *Z. angew. Chem.*, 1902, p. 50, and supplied by Hugershoff, at Leipzig, are very efficient. Here the nitrogen peroxide is absorbed, and the quantity of non-absorbed gases is measured by means of an aspirator. The junctions of the single parts of the apparatus cannot be made by india-rubber tubing, as this is acted upon by the gases, whose composition is thereby altered.[1] The single parts of the apparatus must be either connected by ground-glass joints, lubricated by liquefied phosphorus pentoxide, or by Ludwig's platinum joint (*Ber.*, 1868, p. 232), made by rolling over the point of junction of the two glass tubes (which must be of equal diameter) a platinum sheet, 0·05 mm. thick, and passing over this a piece of india-rubber tubing, which by means of cords presses the platinum tightly against the tubes. When the absorption is finished, the liquids contained in the apparatus are emptied into a stoppered glass bottle, well shaken to be evenly mixed, and measured samples are taken out, in which the total nitrogen is estimated by the nitrometer.

Raschig recommends decinormal caustic-soda solution as absorbent. Lunge and Berl, as well as Grau and Russ (*Chem. Zentr.*, 1907, i. p. 1172), are against this, as about baryta solution.

Warburg and Leithäuser (*Ann. Physik.*, xxviii. p. 313; *Chem. Zentr.*, 1907, i. p. 1173; 1908, i. 922) examine the gases in question by observing their absorption spectra.

Baudisch and Klinger (*Ber.*, 1912, p. 3231) pass air into nitric oxide in contact with solid potassium hydrate; there is an instantaneous formation of N_2O_3, which at once combines with potash, so that the formation of NO_2 is entirely excluded. The operation is performed in a gas pipette, charged with rods of caustic potash and a little water; the air, before admission, is freed from CO_2, and the NO is calculated from the ensuing contraction, of which four-fifths are due to the previously present NO, and one-fifth to the oxygen consumed for the oxidation.

Treatment of the Nitrous Vapours obtained by the Oxidation of Atmospheric Nitrogen.

Page 249. *Processes of the Badische Anilin- und Sodafabrik.*—The German patents for the process mentioned in the text as Ger. P. appl. B52866 is No. 237562.

The U.S. P. 1029528 of Bosch, Keller, and the Badische Anilin- und Sodafabrik refers to the trouble caused in the absorption of the nitrogen oxides formed by the electric flame-arc by towers fed with milk of lime, which in course of time get stopped up. This is avoided by introducing the milk of lime by means of squirting-jets into empty towers, which may have comparatively small dimensions. There is much less power required in this case than when employing towers filled with solid materials. For working the squirting-jets, in lieu of compressed air, part of the gases containing the nitrogen oxides may be employed after previous compression. Milk of lime of 6° Bé. has been found suitable for this purpose peroxide by heating. It can be sent out in iron vessels.

Further patents belonging to the Badische: Schönherr and Brode, U.S. P. 1039325; Schönherr, U.S. P. 1046212.

The Ger. Ps. 220539, 223026, and 223556 of the Badische describe the conversion of nitrites into nitrates. Mixtures of nitrites and nitrates, such as are obtained in the oxidation of atmospheric nitrogen, are treated with nitric acid; the escaping nitrous vapours are mixed with so much oxygen that the proportion of total oxygen to the combined oxygen is as nearly as possible $= 5 : 2$, and the gases are absorbed in water, whereby concentrated nitric acid can be obtained. The B. Ps. are 11274 and 30502, of 1909; the Fr. P. 411674.

Page 251. *Further Details on Schlarb's Process mentioned in the text.*—Of all metals coming into question, only iron aluminium, and chromium yield nitrates, which on heating with water furnish nitric acid without partially splitting this up. When heating at ordinary pressures, the nitric acid commences to distil at 115° to 125°. By gradually raising the temperature to 145°, so much nitric acid is driven out that basic nitrates of the formulæ $M_2(OH)_5(NO_3)$ or $M_4(OH)_9(NO_3)_3$ are formed. If the nitrate liquors are heated in a vacuum, *e.g.* up to 20 mm., the nitric acid commences to distil at 55° to 60°, and the distillation is finished at 75° to 85°. It can be driven out almost completely, as the oxides remaining behind still possess considerable absorbing power.

The same inventor (Schlarb's Ger. Ps. 243839 and 243892; Fr. P. 422751; Austr. P. appl. 2427 of 1911) obtains concentrated gaseous N_2O_3 from dilute nitrous gases, obtaining at the same time nitrates, by treating part of the nitrous gases as described in the last-mentioned patent, absorbing another part by alkalies or alkaline earths, and allowing the nitrate

(Ger. Ps. 244840, 240712, Pauling's B. Ps. 14121 and 14122, 1911; his U.S. Ps. 1057977 and 1061630), pass the gases formed in the electric combustion of air, after traversing an absorbing apparatus acting in the well-known way, through sulphuric acid, and employ the nitrous vitriol thus obtained for drying the cooled gases of the reaction in front of the oxidising space. This acid is then brought again to the concentration required for oxidising the remaining gases by the heat of the furnace gases. The nitrous gases, remaining after the previous oxidation and intensive absorption, are mixed, according to whether they contain an excess of NO or of NO_2, with part of the gases leaving the oxidising space, or else with a corresponding portion of the non-oxidised furnace gases, in such proportions that for each NO there is a molecule of NO_2 present, or *vice versa*. The gaseous mixture is exposed to absorption by alkaline absorbents, sulphuric acid, or similar reagents. The sulphuric acid, after being saturated with NO and NO_2, or N_2O_3, is denitrated in special apparatus, then again concentrated and again used for absorption, conducting the nitrous gases coming from the denitrating apparatus into the principal absorbing apparatus.

The Farbwerke vorm. Meister, Lucius, and Brüning, at Höchst (B. Ps. 15948 and 19032, 1911; Ger. P. 244362; Fr. P. 428657; Aust. P. 59154) prepare pure nitric oxide by the electrolysis of dilute nitric acid, containing nitrous acid, employing for the cathodes carbon (graphite) or platinum and its alloys. The NO produced can be transformed by dry oxygen or air into NO_2, absolutely free from nitric acid, which can be condensed and sent out in that shape. The apparatus serving for the carriage of liquids in the absorbing-apparatus are worked with compressed oxygen, in lieu of compressed air, and the oxygen coming out of the apparatus is carried back into the absorbing system, together duced into the absorbing chambers, the other part being introduced into the chamber in the hot state, regulating the gaseous currents meeting in the chamber in such a way that a mixture of equal molecular proportions of NO and NO_2 is formed.

Guye (U.S. P. 1057052) compresses the nitrogen oxides, diluted with nitrogen and oxygen, to about 6 atmos., and passes the gases into a heat-exchanging apparatus, where they are cooled by expansion, so that the nitrogen oxides separate out. They are then treated with a solvent, *e.g.* carbon tetrachloride, which solidifies only below $-50°$ and boils over $+50°$; it is separated from the nitrogen oxides by distillation.

Heinz (*Z. angew. Chem.*, 1913, i. p. 421) recommends for the condensation of nitric acid made from air, and for similar purposes, the "cellular bodies," made by the Deutsche Steinzeugwarenfabrik at Friedrichsfeld, i.B., as very efficient.

Briner and Durand (*Comptes rend.*, 1912, clv. 1495) examined the action of temperature on the equilibrium between the nitrous acid and nitric acid, formed from nitrogen oxides and water. In the action of water on N_2O_3, the lowering of the temperature and the increase of pressure of the NO promote the formation of HNO_2.

Knowles (Ger. P. 261306) describes the purification of electrolytically generated gases by means of catalytically acting substances.

The Norsk Hydro-Elektrisk Kvaelstofaktieselskab (U.S. P. 1197295; Norw. P. 23068) split up mixtures of acids, one of which is sulphuric acid, by heating them to 80° to 100° with sulphuric acid, the concentration of which is not essentially greater than that of the sulphuric acid contained in the mixture. The same firm (Ger. P. 284042), in order to obtain lime specially adapted for absorbing nitrous gases at 300° to 400°, burns limestone at temperatures not exceeding 700° to 750°, by the excess of heat of the nitrous gases intended to be absorbed, which have

Swed. P. 40830; Swiss P. 72824) combines the direct absorption of the gas in water with a concentration of the dilute NO escaping from the absorption apparatus, by absorption in alkalies and subsequent decomposition of the nitrogen compounds formed by oxides, dioxides, or other compounds of the metals of the alkalies, the alkaline earths, or silica.

Hale (B. P. 21724, 1911) extracts the nitric acid from kieselguhr, etc., in which it had been absorbed, by concentrated sulphuric acid, which at the same time acts as a heating- and water-abstracting agent; the sulphuric acid is recovered from the residue by washing. The same (Fr. P. 477726) absorbs the nitrous vapours in a solution of sodium carbonate, and decomposes the sodium nitrate and nitrite thus formed by heating the solution with oxides or hydroxides of heavy metals of alkaline earths. By this treatment the nitrous gases are obtained in a much more concentrated form, and the alkali is recovered in a form fit for further absorption of the dilute gases. The production of pure alumina from bauxite may be combined with this process of concentrating nitrous gases.

C. L. Richert von Koch (Fr. P. 435733) avoids the decomposition of the nitrogen oxides formed at high temperatures by conducting the gaseous mixture from the furnace through a narrow channel, cooled by water on the outside, into a chamber kept at reduced pressure. If the source of heating had been an electric flame-arc, this is allowed to project to some extent into the low-pressure chamber.

Schloesing (B. P. 22119, 1913; Fr. Ps. 441607 and 460328; U.S. P. 1062295) absorbs hot, dry, nitrous gases by lime in such a way that their heat is as much as possible utilised in the various stages of the process. This is especially carried through when preparing calcium nitrate from atmospheric the nitrous vapours present in gases coming from an electric furnace are absorbed by quicklime at 300° to 400°, the quicklime being produced by burning limestone by means of the hot gases containing the nitrous vapours.

Canadian patents for the treatment of the lower nitrogen oxides: Berneck (142468 and 142469), Moest (142470), Canada Explosives Co. (142472).

Moscicki (U.S. Ps. 1046212 and 1097870) employs an absorbing-chamber shaped as a right angle, with several perpendicular, sieve-holed diaphragms. The small compartments thus formed are filled with pieces of quartz or glass, 2 to 4 in. long and 1 to 4 in. thick, covered by a holed dividing plate. The gas passes horizontally through the perforations of the diaphragms, from the front to the back. The compartments are systematically rinsed by means of compressed air, so that a highly concentrated acid is obtained.

J. A. Hart (B. Ps. 29391, 1910; 27654, 1912) employs for the mutual action of gases and liquids a drum into which the gas enters tangentially, and the washing liquid from below.

The Production of Nitric (and Nitrous) Acid from Ammonia.

We add to the enumeration of theoretical investigations on the oxidation of ammonia or ammonium salts, on page 253 of the text, some data, especially from the older literature of this subject.

Dammer, in his *Handbuch der Anorganischen Chemie*, 1894, ii. p. 53, quotes the old investigations of Fourcroy, Henry, and Bence Jones. Schönbein worked on this subject during the years from 1845 to 1867. Weith (*Berl. Ber.*, 1874, pp. 1481 and 1745) oxidised ammonia by ozone or hydrogen peroxide to ammonium nitrate. Twenty years later Siemens and Halske took the Ger. P. 85103 for the application of

2565), and by Donath and Indra (*Die Oxydation des Ammoniaks zu Salpetersäure und Salpetriger Säure*, 1913).

The oxidation of ammonia by free oxygen with the aid of contact substances was first studied by Kuhlmann in 1839 (*Liebig's Ann.*, xxxix. p. 281), and later on by Schönbein (quoted by Dammer, *loc. cit.*). Warren, in 1891, produced ammonium nitrite by passing a mixture of ammonia with oxygen or atmospheric air over platinised asbestos, heated to a dark-red heat (Donath, *Z. Schiess- und Sprengw.*, 1916, p. 170).

Kochmann (*Arb. d. pharm. Inst.*, Berlin, 1911) worked with several catalysers.

Oesterheld (*Z. anorg. Chem.*, 1914, lxxxvi. pp. 103-142) examined in detail the reactions taking place in the electrolytic oxidation of ammonia.

Meneghini (*Gazz. Chim. Ital.*, 1912, xlii. p. 126; xliii. 1, p. 81; *J. Soc. Chem. Ind.*, 1912, p. 383; 1913, p. 230) passed a mixture of NH_3 with rather more air than corresponds to the reaction

$$4NH_3 + 5O_2 = 4NO + 6H_2O,$$

at a velocity of 20 litres per hour, over various catalysers at temperatures between 300° and 650°, and estimated the percentage of the oxygen entering into the reaction. The action of the catalysers decreased in the following series. 1. Pyrites cinders, containing 0·53 per cent. copper. The reaction commences below 300°; thick vapours are given off, and 65 per cent. of the oxygen is consumed at 400°, 99 per cent. at 550°. 2. Chromium oxide. 3. Mixtures of the oxides of neodymium, praseodymium, and lanthanium. White vapours are formed at 375°, and the oxygen is completely consumed at 650°. 4. Cerium oxide; 85 per cent. of the oxygen is consumed at 650°. 5. Pyrolusite, containing 80 per ordinary temperatures by the *catalytic action* of various substances were made by N. Smith (*Proc. Chem. Soc.*, 1906, p. 39); Sestini (*Z. angew. Chem.*, 1904, p. 1380; 1905, p. 823); Marshall (*Chem. Zentr.*, 1905, i. 559); Kempf (*Ber.*, 1905, p. 3966); Levi and Migliorini (*Gazz. Chim. Ital.*, xxxviii., ii. p. 10; *Chem. Zentr.*, 1908, ii. p. 929); Donath (Donath and Indra, *loc. cit.*, p. 92); Traube and Biltz (*Ber.*, 1904, p. 3130; 1906, p. 166); Loew (*J. prakt. Chem.*, N. F., xviii. p. 298; Schoenewald (quoted by Traube, *Ber.* 1905, p. 828); Andersen (*Z. Elektrochem.*, 1916, p. 441).

Electrolytic Oxidation of Ammonia.—Donath and Indra (*loc. cit.*, pp. 92 *et seq.*) mention the older literature on this subject, and describe in detail the experiments of Frenzel and Drechsel (*J. prakt. Chem.* [2], xxii. p. 476); Fichter and Kappeler (*Z. Elektrochem.*, xv. p. 937); Fichter (*Chem. Zeit.*, 1912, p. 606; *Z. Electrochem.*, xviii. p. 647); Marshall (*Journ. Chem. Soc.*, lix. p. 777); Losanitsch and Jovitschitsch (Danneel, p. 216); F. C. G. Müller (*Chem. Zentr.*, 1911, i. p. 626); Millot (*Bull. Soc. Chim.* [2], xlviii. p. 610); Brochet and Boiteau (*ibid.* [4], v. p. 667); Scagliarini and Casali (*Chem. Zentr.*, 1913, i. p. 994).

Moldenhauer (*Z. angew. Chem.*, 1914, i. p. 334) reports on the experiments made by Wehrheim on the catalytic combustion of ammonia, hydrocyanic acid, and cyanogen into nitric oxide.

According to Scagliarini (*Gazz. Chim. Ital.*, xliii. 1, p. 30; *Chem. Zentr.*, 1913, i. p. 1263), by the anodic oxidation of ammonia in acid solutions in the presence of silver salts only nitric acid is obtained. According to his further experiments (*Gazz. Chim. Ital.*, xliv. 1, p. 543; *Chem. Zentr.*, 1914, ii. p. 1024), in alkaline solutions also nitrous acid is formed. The presence of ammonia in higher concentrations impedes its

$NH_3 \rightarrow HNO_2$; whilst at lower concentrations also the reaction $NH_3 \rightarrow HNO_2 \rightarrow HNO_3$ is going on, as Müller and Spitzer (*Ber.*, 1905, pp. 778 and 1188) had observed, in the presence of copper salts. The yield of nitrous acid increases with the temperature; at 52° it attains a maximum, and at 78° it decreases again to one-fourth. Concerning the influence of catalysers, argentic sulphate up to a concentration of 1·5 g. causes an increased formation of nitrous acid; concentrations over 1·5 g. have no further influence.

A discussion upon the economical aspect of the production of nitric acid or ammonium nitrate from ammonia (with special regard to the Ostwald process) has been carried on by Dieffenbach (*Chem. Ind.*, 1914, p. 265); Uhde (*Chem. Zeit.*, 1914, p. 1015); Dieffenbach (*ibid.*).

Bacterial Nitrification of Ammonia (Donath and Indra, *loc. cit.*, pp. 106 *et seq.*).—The discovery of the nitre-forming bacteria is due to Winogradsky (*Compt. rend.*, cx. p. 1013), who found them first in the water of the Lake of Zurich, and then in various soils. Further work on this subject was done by Kaserer (*Chem. Zentr.*, 1907, i. p. 652), and especially by Müntz and Lainé, who cultivated them by vaccination on peat, and then employed them for the transformation of ammonium sulphate.

Page 255. *Technical Processes for the production of Nitric Acid, Nitrates, and Nitrites from Ammonia.*

Donath and Indra (*loc. cit.*) enumerate the following ways of manufacturing nitric acid, etc., from ammonia:—

1. Oxidation of gaseous ammonia, with or without addition of air, by chemical means, by substances giving off oxygen at higher temperatures.
2. Oxidation of gaseous ammonia by atmospheric oxygen at higher temperatures with the assistance of

for working Ostwald's process of converting ammonia into nitric acid have been made at the Lothringen pit, near Bochum, and in connection with the Berlin-Anhaltische Maschinenbau Aktiengesellschaft at Düsseldorf, and at the Erzherzog Friedrich works in Austrian Silesia. According to *Met. and Chem. Engin.*, 1913, p. 438, an English company had been formed, which, according to *Z. angew. Chem.*, 1914, i. p. 48, works with a capital of two million pounds; it then possessed the works at Alby in Sweden, and Odda in Norway, and it was going to spend in Iceland £400,000, and in Norway £600,000, on the Ostwald process, for which a million horse-power was to be employed.

According to a communication (unsigned) in the *Chem. Zeit. Repertorium*, 1913, p. 553, the above-mentioned English company erected six years ago a plant for converting 25 tons ammonia per month by the Ostwald process into 150 tons nitric acid of 36° Bé. The reaction is simply

$$NH_3 + 4O = NHO_3 + H_2O.$$

When passing the mixture of air and ammonia slowly over the platinum contact mass, the yield of nitrogen oxides is only a few per cent.; but when forcing the gases rapidly through, the yield is almost the theoretical one. The temperature is upwards of 300°; the time of contact $\frac{1}{100}$ second. Ammonia gas, liberated in the usual way, is purified by milk of lime from CO_2 and H_2S, mixed with air, and passed through the contact apparatus. This is constructed of cast iron, if lower nitrogen oxides are produced; or of stoneware, if nitric acid is produced. The gases are condensed in a tower lined with stoneware; here water and nitric acid are condensed; the dilute acid is pumped up on to cooling towers, of which five are employed in succession. The acid running off from the second tower shows 36° Bé. There are thirty contact-elements development of the synthesis of ammonia, *e.g.*, by the method of Haber and the Badische Anilin- und Sodafabrik, is the best foundation for an economical conversion of ammoniacal nitrogen into nitric acid, because the ammonia can be employed without purification, and the cost of plant and working is not large. A nitric-acid plant for producing 10,000 tons of 53 per cent. nitric acid per annum would not cost more than £22,500, and the total cost of producing ammonium nitrate would be 1276 marks (say £50) per ton of the nitrogen contained therein.

The production of ammonium nitrate (or calcium nitrate) for fertilising purposes would also be more profitable for coke-works, utilising the by-products, than that of ammonium sulphate. This fact is also mentioned in Kochmann's pamphlet, *Deutscher Salpeter* (Berlin, 1913), where it is stated that the additional profit in catalytically oxidising ammonia against the manufacture of ammonium sulphate at a coke-works near Bochum was from 25 to 39 per cent. The "Lothringen" pit produced in 1908, 695 tons; in 1909, 1081 tons; in 1910, 1237 tons; in 1911, 1495 tons.

The Farbwerke vorm. Meister, Lucius, and Brüning, at Höchst (B. P. 3662, 1913; Fr. P. 45384; Ger. P. 286751), burn a homogeneous mixture of ammonia and air, containing about 10 to 14·5 per cent. NH_3, and only so much oxygen as is required for the oxidation of ammonia into the desired nitrogen oxides, in presence of a catalyser (platinum-asbestos); the nitrogen oxides and the water are separated by cooling, etc., and pure nitrogen remains behind. According to their B. P. 28737 of 1913, an indifferent gas, like nitrogen, is to be introduced into the mixture of NH_3 and air, in which case the proportion between NH_3 and O must remain that which is required for the combustion of NH_3. The U.S. Ps. 1096392 oxygen, whereby higher concentrations of the nitrogen oxides are obtained.

Orloff (*J. Russ. Phys. Chem. Soc.*, 1908, p. 659) employs a bright red-hot copper shaft as catalyser.

Landis (U.S. P. 1173524) produces gases containing over 6 per cent. of nitrogen oxides, for use in the manufacture of sulphuric acid, by catalysis of a mixture of ammonia and air (The patent is assigned to F. S. Washburn.)

The Verein chemischer Fabriken at Mannheim (B. P. 12600, 1914; Fr. P. 492567) forces the mixture of air and ammonia through the catalyser at a pressure superior to that of the atmosphere, *e.g.* by means of a perforated disk placed behind the catalyser. Their Aust. pat. appl. is A. 4644-14.

Meigs (U.S. P. 1120960) produces nitric acid, together with sulphuric acid, by burning sulphur or a sulphide ore, whereby a mixture of SO_2 and N is produced, combines N and H by the electric current to NH_3, oxidises the NH_3 in aqueous solution into dilute nitric acid, and the SO_2 by ozone into SO_3, passes the SO_3 into the dilute nitric acid in order to obtain concentrated nitric acid along with dilute sulphuric acid, and separates the two acids by distillation.

The Berlin-Anhaltische Maschinenbau Aktiengesellschaft (Ger. P. 286991) combine for the production of nitrogen oxides from ammonia by catalysis conduits for the NH_3 gas and the air, which are connected with each other in a fixed way, allowing the gases to be mixed continually in any desired proportion, before they pass on to the chambers containing the catalyser.

Lymn (B. P. 1851 of 1913; Fr. P. 467592) obtains ammonium nitrate or nitrite by oxidising ammonia in producer gas, etc., by means of nitrogen oxides.

The Oesterreichische Verein für chemische und metal-contact apparatus for the oxidation of NH_3.

The Soc. génér. des Nitrures (Fr. P. 474365) describes a complicated product, obtained in the ferro-silicium furnace from bauxite, carbon, and iron, containing Fe, Al, and their compounds with C, Si, Ti, Ca, etc.; this product gets spontaneously heated when exposed to the air in a finely divided, damp state, and without any supply of heat from without reaches temperatures up to 2000°, with evolution of inflammable gases. The product formed is an impure aluminium nitride.

According to their Fr. P. 476121, nitrogen is fixed by ferro-aluminium by adding to 200 kg. of this compound, containing 42 per cent. Al, 40 kg. of calcium carbide (54 per cent.), whereby the theoretical quantity of nitrogen is not merely attained, but even exceeded, viz., 44·75 kg. N = 103·8 per cent.

According to their Fr. P. 483618, the yield of nitric acid by the oxidation of ammonia is increased, if the hot gaseous products of the reaction of NH_3 with air, immediately after passing through catalysers, meet a current of air, oxygen, or nitrogen. Their Ger. P. is No. 238340.

The Badische Anilin- und Sodafabrik (B. P. 9263 of 1913; Ger. P. 280499; U.S. Ps. 1091689 and 1094182 of Hugo Wolff; Fr. Ps. 464285 and 464237) treats the conduits and apparatus for carrying gases containing ammonia to the catalysers, if they consist of materials liable to give up dusty impurities to the gases, by a purifying process, or brings the previously purified gases before entering into the catalysing apparatus into contact only with such metals which do not, like iron and copper, give up dusty impurities to the gases, thus quickly impairing the contact action of platinum. Nickel or alloys containing much of it are suitable for this purpose.

According to their Ger. P. 283824, the catalytic oxidation in order to avoid their sintering in the apparatus, whereby irregular gaps are formed. The pieces may be employed either in a dense or in a porous state; in the former state they are obtained by crushing the fused oxides. Substances permeable for gases may be mixed with them. The hydroxides of iron, manganese, chromium, uranium, etc., may be precipitated from the solutions of the nitrates or sulphates by ammonia or ammonium carbonate. The precipitates are washed, dehydrated, and pressed in moulds; or part of the washed hydroxides is dried at about 250°, mixed with the other moist part, and pressed into the form of cylinders, cubes, balls, etc. Before using them they are heated to 500° to 700°. The B. P. is taken out by J. Y. Johnson, No. 13689, 1914; their Norwegian patents are Nos. 26690 and 26691; Swiss P. 72690.

According to Ger. P. 287009 of the same firm, catalysers are employed, consisting of iron or bismuth, mixed with rare earths; B. P. (by Johnson) 7651, 13298, and 13292 of 1915.

The preparation of nitrogen oxides from ammonia is the subject of a paper in the *Chem. Trade J.*, 1916, xlix. p. 413, of which we here give an abstract:—

In *Metall und Erz* of 22nd January 1916, some particulars are given of the method introduced in a factory at Stolberg, near Aachen. The gaseous ammonia is burnt by contact with red-hot platinum; the nitrogen oxides formed are not transformed into nitric acid, but are sent directly into the lead chambers. The process used is that of Frank and Caro (*vide* our text, p. 257). In the original plant the ammoniacal liquor, supplied in cylindrical trucks, was mixed with milk of lime, and the mixture was pressed into the top of a column apparatus, supplied at the bottom with steam of 0·3 atmospheric pressure. The gaseous ammonia issuing at the top was cooled in a series

The plant was thus much simplified, the attendance minimised, and the capacity raised tenfold to 1250 kg., which suffices to keep several lead-chamber systems going; one combustion unit suffices for producing 10,000 tons per annum of sulphuric acid of 60 per cent. A number of arrangements for avoiding trouble in the process from various causes is described in the original communication.

Manufacture of Ammonium Nitrate from Ammonia.

Donath (*Chem. Ind.*, 1914, p. 513) discusses the proposal of Dieffenbach (*ibid.*, p. 265), according to which ammonia is not to be sold in the shape of sulphate, in which case the sulphuric acid is a dead ballast, but it is to be converted into nitrate, as projected by the Nitrogen-Products and Carbide Company, which at their factory near Odda makes lime-nitrogen (calcium cyanamide) by means of electricity produced by water-power, and which intends making further 200,000 h.p. available for this purpose by utilising the Aura waterfalls near Bergen. The conversion of the ammonia into nitrate was to be effected by the Ostwald process (*suprà*, p. 123), which has been already carried out on a large scale by that firm. Donath points out that Frenzel already, in the year 1910, in a pamphlet, *Die Nutzbarmachung des Luftstickstoffs*, and Dafert in *Oesterr. Chem. Zeit.*, 1912, p. 56, had insisted on the advantages of combining the production of nitric acid from air with the manufacture of lime-nitrogen, and that Dieffenbach had proved that combination to be economical. According to Perlick (*Die Luftstickstoffindustrie, etc.*), the Norwegian factories sold the ammonium nitrate manufactured from lime-nitrogen, at the end of 1911, delivered at Hamburg, for 48 marks; in Berlin 1912, for 50 to 60 marks per 100 kg. A further reduction of prices was expected from a combination of the

Birkeland and Eyde for obtaining nitric acid from atmospheric nitrogen.

On the progress of the industry of oxidising ammonia to nitric acid a report is made in the *Times* Eng. Suppl. of 15th October 1913 (quoted from *J. Soc. Chem. Ind.*, 1913, p. 1008). The carbide works at Odda in Norway were started with ten furnaces, each with a capacity of 7 to 8 tons of carbide per twenty-four hours. Ten more furnaces, of 16 to 18 tons capacity each, have recently been added. The temperature is maintained at 3160°. The electrodes of the older furnaces take 1400 kilowatts, and those of the newer ones 3500 kilowatts. It is stated that the radiation of heat from the new furnaces is less than from a steam boiler. The hot gases from the furnaces are used in the lime-kilns, instead of producer-gas. The annual output, 32,000 tons up till recently, is now 80,000 tons of carbide. Most of this carbide passes directly to the calcium-cyanide works of an associated company, which at the present has an annual output of 80,000 tons, the number of furnaces having been increased nearly sevenfold since the opening of the works three years ago. The nitrogen used is prepared by the Linde process, 100 tons of air being liquefied daily. The furnaces have a capacity of 1 ton each; the nitrogen is supplied through valves in the side, and a current of 60 to 75 volts through electrodes in the centre. After about twenty-four hours at 900°, the carbide is converted into cyanamide, the product containing 20 per cent. of nitrogen. In addition to this, a company formed to acquire the Ostwald process is erecting works for the manufacture of calcium carbide, cyanamide, and nitric acid at Aura (Norway), with an estimated output of 200,000 tons of calcium cyanamide, and has acquired waterfalls at other places in Norway and in Iceland, capable of furnishing power for an annual output of makes the following statements. The "arc process" (in which nitrogen and oxygen are made to combine chemically at the temperature of the electric arc) requires five or six times as much power as the "cyanamide process" (in which calcium carbide is made to combine at a high temperature with nitrogen, forming cyanamide, from which by means of steam ammonia is obtained, which can be oxidised to weak nitric acid by contact processes); the cost of plant for the former is as 16 to 6 for the latter. The present production of nitrogen by the arc process is equal to 32,000 tons per annum, and is confined to Norway; the production of nitrogen by the cyanamide process is equal to 200,000 tons per annum, and is going on in Norway, Sweden, Germany, Austria, Italy, France, Japan, and Canada. The cost of production of nitric acid by the cyanamide process is 70 per cent. of the cost of producing that acid from Chilian nitrate.

According to *Chem. Zeit.*, 1916, p. 14, the "Bamag" (Berlin-Anhaltische Maschinenbau-Aktiengesellschaft) has during the last few years supplied more than seventy apparatus for the manufacture of nitric acid from ammonia, which produce upwards of 12,000 tons NH_3 per annum; further installations for a production of upwards of 17,000 tons NH_3 are in course of erection. In the Ger. P. 286991 of that firm, a device is specified whereby the conduits for ammonia and air to the catalysers are arranged in such a way as to produce a uniform mixture.

Storage and Carriage of Nitric Acid.

Page 258. Prescriptions for the storage of nitric acid, in consideration of the danger in handling it, have been made by the Prussian Government, as reported by *Zeitschrift f. d. ges. Schiess- und Sprengstoffwesen*, 1913, p. 220. The acid has, wherever it is possible, to be provided for receiving and running out acid and conveying it into a pit filled with water. At smaller factories the acid has to be stored in a closed, well-aired space, with windows opening from without. The floor of these spaces must consist of acid-proof, water-tight materials (*not* Portland cement !), and must have a fall towards a collecting pit, where any running-out acid can be diluted or neutralised; it must be provided with water-taps which can be opened from without.

Jordan (Ger. P. 280863) provides vessels for the carriage of acids with a covering of pitch, asphalt-cement, or the like, laid on hot, in the following way. The vessels, made of glass, stoneware, etc., receive three coverings, laid on one after the other, and joined by fusion. The innermost of these is a mixture of bituminous and fibrous substances; the central layer consists of elastic substances such as wool, peat, or the like, and the outside layer of bitumen, mixed with sand or pebbles. Any shocks from without are deadened by the central layer in such a way that they cannot reach the glass. The central layer is protected against any destructive action of the acid by the acid-proof layers, surrounding it on all sides and partly penetrating into it.

Cf. *suprà*, pp. 65 *et seq.*, the experience made with aluminium vessels for the storage and carriage of nitric acid.

According to the official Prussian rules, quoted *suprà* (p. 130), larger vessels (carboys, etc.) must not be filled right up, but an air-space of 2 litres must be left below the stopper. The stoppers or lids of the carrying-vessels must be loosened immediately on arrival, and later on always during warm weather. The packing material must be removed or rendered fire- and acid-proof by impregnation. The carboys must not be emptied by ordinary siphons, but by means of tilting-arrangements, or emptying-apparatus made of india-rubber.

fabrikation describes a siphon for emptying acid carboys, etc., connected with an aspirator. The aspirator consists of two vessels, fixed in a frame one above the other and connected by a tube; their position can be inverted. The top vessel is connected with the siphon by a flexible tube; the siphon is started by allowing water to flow from the top vessel by means of a tap to the bottom vessel. The operation can be repeated by inverting the frame.

For *pumping nitric acid,* Haughton's Patent Metallic Packing Co., 30 St Mary-at-Hill, London, supply centrifugal pumps made of a description of iron completely resisting the acid, and commercially known by the name of *ironac.*

Acid-proof Iron.—According to *Chem. Trade Journ.,* vol. lix. p. 7, an American acid-proof iron, sold by the name of *corrosiron*, and capable of being machined, has shown a maximum loss of 0·58 per cent. when immersed seventeen days in concentrated hydrochloric acid, and a minimum loss of 0·0015 per cent. in an immersion of seven days in nitric acid of various strengths. It is high in silicon, quite brittle, with a fracture like that of ice. Its strength is about half as great as that of cast iron, but it has been strengthened by casting it with bars of iron or steel inside. In making use of it, flat surfaces are avoided and corners are rounded.

Subaqueous tanks for the carriage of nitric acid and other corrosive liquids are proposed by H. N. Morris (B. P. 8370 of 1916; *J. Soc. Chem. Ind.*, 1916, p. 1246).

Statistics on Nitric Acid.

Page 262. According to the *Fiftieth Annual Report on Alkali, etc., Works*, by the Chief Inspector, 1914, pp. 5 and 142, there existed in the year 1913 in England and Ireland 72, nitric acid; exported in 1912, 3077 tons; in 1913, 1370 tons, nitric acid.

Austria-Hungary imported in 1912, 54 tons; exported in 1912, 1251 tons, nitric acid.

The United States, in 1910, produced 68,600 tons nitric acid in 25 works; in 1915, 78,600 tons nitric acid in 52 works, and 112,000 tons "mixed acids" in 37 works.

CHAPTER III

THE PROPERTIES AND ANALYSIS OF THE TECHNICALLY EMPLOYED OXIDES AND ACIDS OF SULPHUR

SULPHUR DIOXIDE.

Page 264. The ultraviolet spectrum of sulphur dioxide has been examined by Garrett (*Phil. Mag.* [6], xxxi. p. 505), and by Baby and Garrett (*ibid.*, p. 512).

Page 265. *Solubility of Sulphur Dioxide.*—Guiselin (*Mat. grasses*, vi. p. 3144; *Amer. Abstr.*, 1913, p. 4048) found that pure, anhydrous sulphur dioxide is more soluble than in water in certain oils, viz., 25 per cent. at 20°, 175 per cent. at −5°. These solutions do not act upon metals, and might therefore be employed in cold-producing machines, and for storing and carrying sulphur dioxide.

Page 268. *Reaction between Sulphur Dioxide and Water at Various Temperatures.*—According to Jungfleisch and Brunel (*Comptes rend.*, 9th June 1913), the final products of the reaction of SO_2 on water at temperatures up to 160° are sulphur and sulphuric acid. The reaction is all the slower the more concentrated is the solution of the SO_2 and the lower the temperature. At low temperatures first hydrosulphurous acid and sulphuric acid are formed:

$$3SO_2 + 2H_2O = H_2S_2O_4 + H_2SO_4.$$

Later on the hydrosulphurous acid decomposes into sulphur reactions.

Förster (*Arb. d. Kais. Gesundheitsamts*, 1914, p. 468; *Chem. Zeit.*, 1915, i. p. 447) investigated the durability of aqueous solutions of sulphur dioxide.

Action of Oxygen on Sulphur Dioxide.—According to Berthelot, the combination of dry gaseous sulphur dioxide with dry oxygen under the influence of strong electric currents produces the crystallised anhydride of persulphuric acid, S_2O_7.

Page 272. *Bactericidal Properties of Sulphur Dioxide and Sulphides.*—A number of investigations on this subject has been made by the German Imperial Board of Trade; abstracted in *Z. angew. Chem.*, 1913, ii. p. 589.

An investigation of the decomposing action of sulphurous acid on some rock-forming minerals has been made by Lotz (*Rauch und Staub*, 1913, p. 279; abstracted in *Chem. Zeit. Rep.*, 1913, p. 568).

Tatlock and Thomson, in a lecture given before the Society of Public Analysts (abstracted in *Chem. Trade J.*, 1914, p. 396), point out that the mere fact of the presence of sulphates in plants in excess of those which have grown in a pure atmosphere is no proof for any damage having been caused to the plants by the acids of sulphur; this they prove by the results of the analysis of plants from various localities. They conclude that such damage can be assumed to have taken place only if, 1st, the percentage of SO_3 is considerably in excess of that which normally occurs in the plants; 2nd, if a leaf or other part of the plant on wetting its surface with water and litmus shows an acid reaction; phenolphthalein is not to be used as indicator.

Page 274. *Detection of very small quantities of Sulphurous Acid*, e.g. in parts of plants damaged by acid smoke.—

of the gas are mixed in a bottle with starch solution, which is made to moisten the walls of the bottle all over; then $\frac{1}{1000}$ normal iodine solution is run in, until a blue colour appears. If the gas contains 4 to 10 vols. SO_2 in a million volumes, the colour appears when 70 to 80 per cent. of the SO_2 have been consumed.

Denigès (*Bull. Soc. Pharm., Bordeaux*, liv. p. 145; *J. Soc. Chem. Ind.*, 1915, p. 149) dips a glass rod into a solution of mercuric sulphate, and exposes it to the air to be tested. If any SO_2 is present, characteristic crystals of mercurous sulphate are formed.

Page 276. *Quantitative Estimation of Sulphurous Acid.*—Kedesdy (*Chem. Zeit.*, 1914, p. 601) confirms Lunge's statement that methyl-orange changes its colour exactly at the point where the bisulphite has been formed:

$$H_2SO_3 + NaOH = NaHSO_3 + H_2O.$$

When employing phenolphthalein for titrating free sulphuric acid, the red colour only appears when all the sulphurous acid has passed over into the normal salt, Na_2SO_3; but in this case the change of colour is quite gradual, and the titration with this indicator is not exact. He, therefore, prefers oxidising the sulphurous acid by hydrogen peroxide into sulphuric acid, which is going on smoothly at the ordinary temperature, and then titrating with normal caustic-soda solution and methyl-orange. This method is especially suitable for estimating the sulphurous acid in fuming oil of vitriol. In this case a first titration is made with methyl-orange and normal caustic-soda solution up to the point where a yellow colour sets in, which shows that apart from sulphate also the bisulphite has been formed; only then hydrogen peroxide is *liquid sulphur dioxide* can be tested, which, according to *Papierzeitung*, 1892, No. 62, sometimes contains up to 20 per cent. sulphuric acid. A special apparatus for the analysis of liquid sulphur dioxide is described in Fr. P. 435763 of the Comp. ind. d. proc. R. Pictet (*J. Soc. Chem. Ind.*, 1913, p. 412).

Sander (*Chem. Zeit.*, 1914, p. 1057), on titrating sulphurous acid with decinormal caustic-soda solution, found that the values obtained with methyl-orange as indicator agree very well with those obtained by titrating with iodine, but the application of phenolphthalein as indicator gave no good results. But since even with methyl-orange the change of colour is not so sharp as in the case of other acids, he prefers oxidising the SO_2 by perfectly neutral hydrogen peroxide, and titrating the sulphuric acid formed, which can be done with the utmost accuracy. In *Z. angew. Chem.*, 1915, p. 10, he recommends oxidising the SO_2 by boiling with a solution of mercuric chloride in very dilute solution.

Jamieson (*Amer. J. Soc.*, xxxviii. p. 166) titrates sulphurous acid with potassium iodate in the presence of hydrochloric acid and a little chloroform (method of Andrews).

Determination of Sulphur Dioxide and Trioxide in Flue-gases.—Nestell and Anderson (*J. Ind. Eng. Chem.*, 1916, p. 258; *J. Soc. Chem. Ind.*, 1916, p. 474) draw the gases through a Hawley filter (*J. Soc. Chem. Ind.*, 1912, p. 1183), in order to retain sulphur trioxide, and then through a wash-bottle containing *N*/10 sodium carbonate and hydrogen peroxide, to absorb the sulphur dioxide. If the flue-gases are hotter than 450°, the sampling-tube inserted in the furnace or flue must be cooled, or the gases must be aspirated very rapidly in order to prevent the oxidation of SO_2 to SO_3.

The estimation of sulphur dioxide (*and sulphur trioxide*) *in burner-gases* is described in our text, pp. 571 *et seq.*

If in a solution more SO_2 occurs than in bisulphite, a first titration is made with normal caustic-soda solution and methyl-orange until the red colour is just destroyed, then phenolphthalein is added and the titration with soda solution is continued until a red colour appears. Every cubic centimetre of soda solution used in the first instance (with methyl-orange) shows per cubic centimetre of the liquid 0·06407 g. SO_2 in the free state; the cubic centimetres afterwards used on titrating with phenolphthalein show per cubic centimetre 0·06407 g. combined SO_2, as $NaHSO_3$, therefore half of it=0·032035 g. as a "semi-free" sulphurous acid.

The titration of sulphites can also be performed with a permanganate solution. According to Milbauer (*Z. anal. Chem.*, 1909, p. 17), accurate results are only obtained if the permanganate solution (of which 1 c.c. should indicate 1 mg. SO_2) is employed in tenfold excess; then 20 vols. per cent. of concentrated sulphuric acid is added, then the sulphite solution (of which 1 c.c. should contain at most 1 mg. SO_2), and the excess of permanganate is retitrated with oxalic acid, ferrosulphate, or hydrogen peroxide. The titration with potassium iodide and thiosulphate does not yield satisfactory results. Traces of bromine or iodine promote the oxidising process.

Analysis of Liquids used for the manufacture of Sulphite Cellulose.—In these, first, the total SO_2 is found by running the sulphite solution, which usually contains about 50 g. SO_2 per litre, after diluting it to one-half, from a burette into 25 c.c. acidulated decinormal iodine solution until the colour has been discharged. The quantity of iodine employed oxidises 0·08009 g. SO_2; hence that quantity of SO_2 is contained in the free and fixed state in the consumed quantity of sulphite liquor. The quantity of free and "semi-free" sulphurous acid, *i.e.*

dride at the moment of being formed has the simple formula SO_3.

Page 281. *Pyrosulphuric Acid.*—The pure compound, $H_2S_2O_7$, technically designated as fuming O.V. containing 45 per cent. SO_3, as well as those acids which contain only a little H_2SO_4 or SO_3, together with pyrosulphuric acid, viz., "Fuming O.V. from 40 to 60 per cent.," are solid; but those acids which contain less than 40, or from 60 to 70 per cent. SO_3, are oily liquids. Above 70 per cent. the fuming O.V. is again solid, up to 100 per cent. SO_3.

E. Moles (*Ann. Fis. Quim.*, 1915, xiii. p. 134; *J. Chim. Phys.*, 1915, xiii. p. 207; *J. Soc. Chem. Ind.*, 1915, p. 960) describes solutions of selenium and tellurium in sulphuric anhydride, their influence on the solidifying-point of SO_3 and their electrical conductivity.

Page 286. *Monohydrated Sulphuric Acid.*—Donk (*Chem. Weekblad*, x. p. 956; *Abstr. Am. Chem. Soc.*, 1914, ii. p. 1926) has obtained crystalline sulphuric-acid monohydrate, H_2SO_4, H_2O, by mixing 40 parts of lead or barium sulphate with 60 parts of 85 per cent. sulphuric acid, and setting the mixture away at 0° overnight. A portion of the crystallised mass thus obtained is then used for seeding or inoculating a new portion of 85 per cent. sulphuric acid, which has also been kept overnight at 0°, when the acid rapidly crystallises. The crystals are monoclinic. Crystallised H_2SO_4 is similarly obtained by seeding 99·9 per cent. sulphuric acid with a portion of a solidified mixture of 60 g. 99·9 per cent. sulphuric acid and 40 g. of lead sulphate. Crystallised H_2SO_4 is more difficult to obtain than crystallised H_2SO_4,H_2O, and is not formed if the acid is weaker than 99·50 per cent.

Jorissen (*Weekblad*, x. p. 962; *Am. Abstr.*, p. 3540) states that highest concentrations of sulphuric acid any extrapolations are of doubtful value.

Page 287, line 13. The theoretical vapour density of real SO_4H_2 is = 3·3862 (not 3·862, as printed in the text).

Page 289. The work of Pickering on the solidifying-points of mixtures of water and sulphuric acid has been extended by Giran (*Bull. Soc. Chim.*, xiii. p. 1049, of 1913). He established the solidifying-points of mixtures containing from 68 to 70 per cent. H_2SO_4, and found a hydrate, $H_2SO_4,2H_2O$, as well as two eutectic points. He further investigated the solidifying-points of mixtures of water with SO_3 beyond H_2SO_4, and found a maximum at +35°, *i.e.* the fusing-point of pyrosulphuric acid.

Page 295. *Baumé Hydrometer.*—According to the U.S. Bur. Stand., No. 69, quoted in *Chem. Abst. Am. Chem. Soc.*, 1916, p. 1720, the Bureau in 1904 adopted for liquids heavier than water the formula: Degrees Bé. = 145 to 145/*d* at 60/60° F. This was confirmed in 1916.

Page 302. The tables of the density of sulphuric acid by Sidersky (*Chem. Trade J.*, 1916, lix. p. 416) and by Holler and Peffer (*J. Amer. Chem. Soc.*, 1916, xxxviii. p. 1021) contain nothing new.

Page 313. *Vapour-tensions of Dilute Sulphuric Acids.*—Hacker (*Ann. Physik.* (iv.), xxxix. p. 1338, of 1912) gives a mathematical derivation of the variations of the vapour-tensions of dilute sulphuric acids by the temperature, the results of which agree very well with the observed pressures.

The *viscosity* of sulphuric acid has been examined by Dunstan and Wilson (*Trans. Chem. Soc.*, 1907, xci. p. 85);

at various temperatures have been determined by Morgan and Davis (*J. Amer. Chem. Soc.*, 1916, p. 855).

Page 320. *Action of Sulphuric Acid on Platinum.*—This subject is specially treated in our text, pp. 1150 *et seq.* We here quote some statements not contained there.

According to Marie (*Comptes rend.*, 1907, p. 145; 1908, p. 475), in the presence of oxidising substances, like persulphate, bichromate, permanganate, or chlorate, platinum is sensibly dissolved already at ordinary temperatures, even by dilute sulphuric acid.

Impure platinum is sometimes more, sometimes less acted upon by sulphuric acid than pure platinum, according to circumstances. According to experiments made by Heraeus (*Chem. Zeit. Rep.*, 1891, p. 36), an alloy of 90 per cent. platinum with 10 per cent. iridium, on boiling for forty days with sulphuric acid, lost only half as much weight as pure platinum; an alloy of 95 per cent. platinum + 5 per cent. iridium lost three-quarters as much as pure platinum. Similar results were obtained by Scheurer-Kestner (*Comptes rend.*, Nov. 1875; *Dingl. polyt. J.*, ccxxi. p. 82). According to Délépine (*Comptes rend.*, cxlii. p. 631), the advantage of the alloy of 90 per cent. platinum with 10 per cent. iridium over pure platinum decreases after boiling for eight to ten hours.

Page 328. *Action of Sulphuric Acid upon Iron and Steel.*—Fawsitt and Powell (*J. Soc. Chem. Ind.*, 1914, xxxiii. pp. 234 *et seq.*) have made a very extensive study of the action of sulphuric acid upon those metals, the results of which they summarise as follows:—

1. Concentrated sulphuric acid acts at the ordinary temperature on steel and on some kinds of cast iron, the

for each 10° C. rise of temperature.

4. The rate of reaction depends on the concentration of the acid, but for small dilutions the ratio of hydrogen to sulphur dioxide in the mixture of gases evolved remains almost unchanged.
5. Although the rate of reaction depends to a certain extent on the composition of the sample of iron, as indicated by the large difference between steel wire and pig iron, an important factor governing the reaction with any one sample appears to be the condition of the surface of the iron.
6. Laboratory experiments on the rate of reaction were found to give results similar to those obtained on the large scale.
7. For the carriage of iron drums containing sulphuric acid, it is possible to calculate the conditions for safe carriage in any particular instance.

Aitchison (*Trans. Chem. Soc.*, 1916, cix. p. 288) investigated the action of 10 per cent. sulphuric acid on steels alloyed with vanadium, chromium, tungsten, nickel, cobalt, and manganese. Vanadium does not pass into solution until the steel contains 5·4 per cent. of the metal, showing that up to that point the whole of the vanadium is present in the state of carbide, which is not attacked by sulphuric acid under the conditions of the experiment. Chromium is present both in solid solution and in the carbide, and the latter is slightly attacked. Alloys containing large percentages of chromium, however, give up very little to the acid. Tungsten is entirely present as carbide up to 11·5 per cent., and this is not attacked by acid. Nickel, on the other hand, is present only in solid solution until high percentages are reached, whilst cobalt is contained only as carbide.

concentrations absorb:

Pure H_2SO_4	=	100 per cent. H_2SO_4	. 3·5 vols. NO.
$H_2SO_4+2.3H_2O$	=	68·5 „ „	. 1·7 „
$H_2SO_4+6.5H_2O$	=	45·5 „ „	. 2 „
$H_2SO_4+9H_2O$	=	37·3 „ „	. 2·7 „
$H_2SO_4+17H_2O$	=	24·3 „ „	. 4·5 „
Pure Water	=	0 „ „	. 7·5 „

Page 335. The *Constitution of Chamber Crystals* is discussed by Biehringer in *Z. anorg. Chem.*, 1916, iii. p. 532. At temperatures from 10° to 15° their formula approaches most to nitroso-sulphuric acid, at 28° to 30° to nitro-sulphonic acid.

Page 349. *Blue Acid.*—On this point Manchot has made a number of investigations (*Z. angew. Chem.*, 1910, p. 2112; 1911, p. 13; 1912, p. 1055). Contrary to Raschig, who on passing nitric oxide into sulphuric acid had observed a reddish colour and a much greater solubility than that stated by Lunge (*vide* our text, p. 331), Manchot could not, even at the temperature of liquid air, find that colour, nor a greater solubility of NO than that observed by me. He has no doubt that the sulphuric acid employed in Raschig's experiments contained a trace of iron, which would explain the red colour; in this case, according to Manchot and Huttner (*Lieb. Ann.*, ccclxxii. p. 152), a crystallising compound of equal molecules of $FeSO_4$ and NO is formed, whilst a solution of NO in the presence of ferric sulphate in sulphuric acid contains 2 mols. NO to 1 mol. Fe in chemical combination. Manchot also objects to the theory of Sabatier (*Comptes rend.*, cxxii. pp. 1417, 1479, 1537; cxxiii. p. 255), according to which the coloured solutions of nitric oxide and copper or iron sulphate contain salts of "blue acid," to which Sabatier gives the formula:

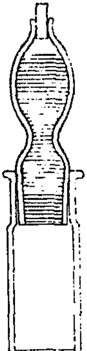
indefinitely repeated. The first reddish tint appears at −40°; at −80° the colour is intensely carmine red, and does not any more change if the temperature is further lowered. By this play of colours the blue acid can be much more easily discovered than it had been hitherto possible. The question now arises whether the blue acid contains any sulphur at all; but it was not possible to obtain a blue solution in the absence of sulphuric acid. Further experiments showed that sulphurous acid is not required for the formation of the blue acid; this acid is formed from sulphuric acid by every other reducing agent, and therefore cannot be a derivative of sulphurous acid, but probably it contains in its molecule sulphuric acid, probably also water, since no very high concentration of sulphuric acid is required for its formation. Nor is it formed by bringing nitric oxide into contact with concentrated sulphuric acid, as shown before. The reducing agent does not act on the oxygen combined with sulphur, but on that combined with nitrogen. In any case the blue acid is a compound of H_2SO_4 with an oxide of nitrogen, probably with one in which the proportion between N and O is intermediate between 1 : 1½ (as in nitrous acid) and 1 : 1 (as in nitric oxide).[1] In any case, it is a complicated compound in which more than 1 mol. NO is present for every molecule of NO_2, and in which, therefore, the proportion between NO and NO_2 is much more complicated than in N_2O_3. To this assumption also points the change of colour on strong cooling, which accompanies phenomena of dissociation and polymerisation. Moreover, Manchot refutes Raschig's assertions concerning a nitric-oxide compound of cupric sulphate (*loc. cit.*, 1911, p. 160); we do not enter upon this point, as this controversy has no direct interest for the chamber process.

Eng., 1916, p. 353).

Page 356, line 15, the figure 53 should be changed into 53·05.

Page 358. *Analysis of Fuming Oil of Vitriol.*—The principle of this analysis is the following. Its value is essentially due to its percentage of free SO_3. To begin with, the total acidity is determined and calculated as SO_3. Assuming the difference between this and 100 per cent. to be $= H_2O$, each 18·016 parts of H_2O would correspond to 80·07 parts SO_3 for the formation of H_2SO_4. The SO_3 present over and above this 80·7 parts is assumed to be in the free state. But, besides water, other impurities may be present, of which especially SO_2 exercises a considerable influence (*cf.* our text, p. 365), and also solid impurities sometimes occur in sensible quantities. These must, therefore, be estimated and the amount deducted from that of the water.

Page 358. *Weighing the Samples of Sulphuric Anhydride and Fuming O.V. for Analysis.*—Clar and Gaier employ glass bottles, as shown in Fig. 5, 58 mm. high and 17 mm. wide, with a long, ground-in stopper, enlarged at the top into a bulb, closed by a small glass stopper. The bulb is filled with glass wool, slightly moistened, 2 or 3 g. of the fused anhydride or the fuming O.V. is put into the bottle, the stopper is quickly put on, the whole is weighed, the head of the stopper is fastened by putting a strong platinum wire round the contracted place, and the bottle is allowed to slide, head downwards, into an inclined 2-litre flask, containing about 500 c.c. water of 50° to 60°; the



end the bottle is rinsed with water inside and outside; the volume of the liquid, after cooling, is brought by water to 1 litre, and for each test 100 c.c. is taken out and titrated by fifth-normal caustic soda and methyl-orange.

Page 361. A new shape of pipettes for weighing off acids is described by Berl in *Chem. Zeit.*, 1910, p. 428, as being lighter than the other forms. Gavelle (*Monit. Scient.*, 1913, p. 301) weighs the fuming acid in a bulb-tube, the upper, short end of which is bent in an angle; the bottom end is drawn out into a capillary which is fused up after drawing the sample. For exact analyses he sursaturates the acid with sodium carbonate and titrates back with standard acid, with methyl-orange as indicator. He gives new tables for estimating the SO_3 by its specific gravity, and the corrections for temperatures above and below 20°.

Dobriner and Schranz (*Z. angew. Chem.*, 1896, p. 453) dissolve from 6 to 8 g. O.V., contained in a fused-up tube, by smashing the tube in a litre flask containing about 150 c.c. water, and add so much pure dry sodium carbonate, previously weighed, that only 3 or 4 c.c. caustic-soda solution is required for retitrating. By this means the sources of errors caused by the preparation of the standard solution, the burette, etc., are reduced to a minimum.

In *Chem. Trade J.*, 1916, lix. p. 417, it is pointed out that the samples of O.V. must be rendered homogeneous by shaking or by a current of dry air.

Page 363. The figures in the second paragraph should be as follows:—Standard soda solution indicates 0·040035 g. SO_3, and the proportion of free SO_3 and H_2SO_4 present is then read off by means of the following formula:

$$SO_3 = S$$

H_2SO_4 in a high-grade or fuming oil of vitriol is effected by Pór (*Metall und Erz*, 1916, p. 130; *Chem. Zentr.*, 1916, i. p. 903) by diluting the acid and ascertaining the Baumé-degrees of the mixture.

Page 368. *Qualitative Examination of Sulphuric Acid for Impurities.*

A. *Gaseous Impurities.*—Two kg. of the acid (undiluted) are shaken up in a bottle half-filled with it, whereby the air contained in the bottle is saturated with the gases dissolved in the acid. They are tested: 1st, for *sulphur dioxide* by iodide-starch paper; 2nd, for the *gaseous oxides of nitrogen* by potassium-iodide starch paper. Only a great excess of SO_2 would decolorise the paper, turned blue by nitrous gases.

Sulphur dioxide is found by the discharge of the blue colour of faintly blue iodine-starch solution. Or the SO_2 is converted by zinc or aluminium into hydrogen sulphide, and this is looked for by testing with lead paper, or with an alkaline solution of sodium nitroprusside.

Hydrogen Chloride.—Two g. acid is diluted to 30 c.c., and a few drops of silver-nitrate solution are added. The purest sulphuric acid shows no precipitate, but this is formed in ordinary sulphuric acid, into which HCl is introduced by the NaCl present in the nitre.

Hydrogen fluoride is detected by heating the acid in a platinum dish, covered with a glass plate, coated with wax, some figures being scratched into the coating.

Ammonia.—Dilute 2 g. acid with 30 c.c. water, sursaturate with a solution of potassium hydrate (3 or 4 g.), and add 10 to 15 drops of Nessler's reagent; this ought not to produce a yellow or brown-red colour. Krauch found by this test a distinctly yellow colour and opacity, when adding 1 mg. NH_3 to 100 g. concentrated sulphuric acid.

a little, allow to cool, and add a solution of potassium sulphocyanide in excess. To make sure that any red colour appearing is not caused by the nitric acid, a controlling test must be made with the latter.

Venables (*Z. anal. Chem.*, xxviii. p. 699) employs a mixture of cobalt nitrate with strong hydrochloric acid; the blue colour of this solution is changed into green by traces of ferric salts, but not by ferrous salts. According to Kander (*Jahresb.*, 1887, p. 2185), sulphuric acid containing iron dissolves codein with blue colour.

Selenium.—Apart from the tests quoted in the text (p. 376), the following must be mentioned.

A special reagent for selenium is codein (mentioned in the text, p. 376). According to E. Schmidt (*Arch. Pharm.*, 1914, p. 16), a solution of a few milligrams of codein phosphate in 10 c.c. sulphuric acid in the presence of only 1 part of SeO_2 in a million parts of sulphuric acid produces a distinctly green colour, which after standing for a quarter of an hour is changed into deep blue-green. Selenic acid (SeO_3) is not indicated by this or the other reagents, but (as well as SeO_2) by acetylene, which indicates already 0·001 per cent. selenium by a red colour. The addition of a little hydrochloric acid accelerates the secretion of the selenium, which dissolves in the hot sulphuric acid with green colour. The *red* colour of sulphuric acid sometimes observed is usually caused by a very slight percentage of selenium, in cases where in the denitration of Gay-Lussac acid an excess of SO_2 had been applied.

Meyer and Tannek (*Z. anal. Chem.*, 1913, p. 534) prove the presence of small quantities of selenium by sodium hydrosulphite, which reduces it to the colloidal state, producing a deep red colour of the liquid. 0·1 g. of the hydrosulphite is added to 1 c.c. of the faintly acid solution; the colour appears after a few seconds. The solution is then neutralised by solid sodium carbonate in order to prevent the liberation of yellow hydrosolutions containing selenium, when evaporated on a water-bath, lose sensible quantities of SeO_2 by volatilisation. This loss is very considerable in the presence of free hydrogen chloride, and on repeated evaporation with HCl may go up to 80 per cent. of the selenium; it is not reduced by the presence of potassium or sodium chloride.

J. Meyer and W. von Gaon (*ibid.*, p. 29) carry out the quantitative estimation of selenium colorimetrically by measuring the intensity of the colour of iodine, liberated from an acidulated solution of potassium iodide by the selenium dioxide; this colour in dilute solutions is yellow, in concentrated solutions yellowish brown up to blackish brown. The reaction is:

$$H_2SeO_3 + 4HJ = 4J + 3H_2O + Se.$$

In order to obtain the liberated selenium in a colloidal solution, a few drops of a solution of gum arabic are added; otherwise the selenium would be separated in red flakes, very much interfering with the reaction. The comparative measurings of the intensity of colour were made by a Krüss colorimeter with a Lummer-Brodhuhn prism at daylight. In this way selenious acid can be estimated in dilutions of one in a million.

Denigès (*Ann. Chim. anal.*, 1915, pp. 57 and 59) proves selenium by boiling the substance with a few drops of concentrated hydrochloric acid, diluting with the same volume of water, and adding a dilute solution of mercurous nitrate, which produces a characteristic precipitate of mercurous selenite. In case of very small traces the reaction can be carried out on a microscope-glass.

The method of Littmann is described in our text, pp. 1070 *et seq.*

Meunier (*Comptes rend.*, 1916, p. 332) detects selenium by means of Marsh's apparatus.

vol. i. pp. 362 *et seq.* To that volume I also refer for the quantitative estimation of arsenic in sulphuric acid.

Page 375. *Examination for Nitrogen Acids.*—Further communications on the diphenylamine reaction have been made by Tillmans and Sutthoff (*Z. anal. Chem.*, l. p. 433), and by de Jong (*Bull. Soc. Chim.* [3], ii. p. 317).

Quantitative Methods.

Page 377. *Estimation of Hydrogen Fluoride in Sulphuric Acid.*—Ehrenfeld (*Chem. Zeit.*, 1905, p. 440) precipitates both acids as barium salts. The mixture is treated with a measured quantity of calcium dichromate, employed in excess, in hydrochloric acid solution. By this agent the barium fluoride is transformed into barium dichromate, whilst barium sulphate is not acted upon. The excess of bichromate is titrated back in the filtrate.

Estimation of Hydrogen Chloride in Sulphuric Acid.—Ten c.c. of the acid is boiled in a flask; the vapours are conducted over the surface of a little water contained in a flask, which absorbs the HCl, and in this solution it is estimated acidimetrically or by titration with decinormal silver nitrate solution.

Page 377. *Estimation of Arsenic, Iron, and Mercury in Sulphuric Acid.*—Nissenson (*Chem. Zeit.*, 1914, p. 1097) estimates all of these in the same sample of sulphuric acid. The acid is heated on the sand-bath until the nitrous acid is driven out, then diluted with three volumes of water and poured upon zinc (free from iron), contained in a flask. After three hours the metallic sponge is filtered off, washed, and in the filtrate the iron is estimated by titration with permanganate. The residue is dried, mixed with quicklime, and heated in a

Schloesing's Method).—Bowman and Scott (*J. Ind. Eng. Chem.*, 1915, p. 766; *Z. angew. Chem.*, 1916, p. 186) describe some modifications of this method.

Wuyts (*J. Soc. Chem. Ind.*, 1916, p. 149) employs this method also for the analysis of mixed and spent acids, and describes the apparatus which he uses for this purpose.

Letts and Rea (*J. Soc. Chem. Ind.*, 1915, p. 793) describe their modification of that method.

Page 383. *The Nitrometer.*—The nitrometer tap must be examined for its air-tightness. This will frequently have to be secured by a slight greasing with vaseline, taking care that no vaseline gets into the bore and thus comes into contact with the acid, since in this case a very slowly settling froth is formed. It cannot very well be expected that a glass tap should keep permanently tight against strong over- or under-pressure during a long time. It is, however, quite sufficient if, when the tube *a* is perfectly filled and tube *b* is placed at a low level, no air-bubble is visible at the top of *a* after two hours. Better than ordinary ground-in glass taps, close the taps with a circular luting of mercury, according to Göckel (*Z. angew. Chem.*, 1900, pp. 961 and 1238), supplied, *e.g.*, by Alt, Eberhard, and Jäger, Ilmenau.

Even preferable to vaseline for greasing glass joints of all kinds is a mixture of 12 parts vaseline with 1 part paraffin wax, into which, after fusion, 9 parts india-rubber cuttings have been stirred up to complete solution (Dennis, *Gas Analysis*, p. 115).

Japp (*J. Soc. Chem. Ind.*, 1891, lix. p. 894) showed that by suitably placing the "reduction tube" of the gas-volumeter, the readings can be made in such manner that they indicate immediately the *weight* of the gas in question. If, *e.g.*, in a cylindrical reduction tube the point 25 is taken as unit, the not a sufficient degree of accuracy. But Japp's proposal can be carried out more accurately, if an ordinary reduction tube, divided from 90 to 150 c.c., is used and placed at 100. If in the measuring tube the cubic centimetres read off are to indicate milligrams, the mercury in the reduction tube must be placed at 100 times the litre weight of the gas in question, *e.g.* for nitric oxide at 134·02. But Japp's proposal, even in this improved shape, rarely has an advantage over that made by myself, viz., employing for the test such a weight of the substance that on placing the reduction tube at 100, the readings of the measuring tube indicate immediately the percentage sought.

Later on, other authors have constructed apparatus by which gases can be measured without the aid of a thermometer and barometer, *e.g.*, Hempel (*Z. angew. Chem.*, 1894, p. 92); Bleier (*Ber.*, 1897, p. 2733; 1898, p. 236); Bodländer (*Z. angew. Chem.*, 1895, p. 49). The barothermoscope of Salomon (*ibid.*, 1893, p. 376; 1894, p. 686) is rather too complicated for practical use.

Planchon (*Ann. Chim. anal.*, 1915, p. 189; *J. Soc. Chem. Ind.*, 1915, p. 1031) describes a modification of the nitrometer, which he calls "manonitrometer."

Page 386. *Nitrometers for Solid Substances.*—Senften (*Chem. Zeit.*, 1916, p. 39) employs an "agitating vessel" (see Fig. 57, p. 384, at E) of such a shape that the solution of the substance may be prepared in this vessel itself.

Page 389. *Testing Nitrous Vitriol by the Permanganate Method, etc.*—Busvold (*Chem. Zeit.*, 1915, p. 214) states that sometimes erroneous results are obtained by Lunge's permanganate method. This is not the fault of the method itself, but of the fact that the permanganate solution employed in those solution of potassium iodide, and after a few minutes the free iodine formed is titrated with thiosulphate solution. This method is right in principle, but its drawbacks are the necessity of employing several standard solutions, and the expensive use of potassium iodide; *cf.* Lunge and Berl (*Z. angew. Chem.*, 1806, p. 809).

L. W. Winkler (*Chem. Zentr.*, 1915, i. p. 503) also determines nitrous acid by the well-known separation of iodine by that acid; but his process is not intended for nitrous vitriol, but for the examination of polluted water.

Rupp (*Z. anal. Chem.*, 1906, p. 687) oxidises the solution of nitrites (which must not contain upwards of 1 per cent.) by an excess of permanganate solution, with heating, dilutes with water after cooling, acidulates with sulphuric acid, and determines the excess of permanganate by Volhard's method.

B. S. Davison (*J. Amer. Chem. Soc.*, 1916, xxxviii. p. 1683) employs the iodometric method, previously driving out the air by carbon dioxide.

Determination of the Three Nitrogen Acids occurring together.

The proportions of N_2O_3, N_2O_4, and HNO_3 in a mixture of all three acids absorbed by sulphuric acid can be derived from the results of the permanganate titration, combined with estimation of the total nitrogen as NO in the nitrometer, by the following formulæ :—

a = c.c. NO, found in the nitrometer.
b = c.c. O, calculated from the permanganate titration (1 c.c. O = 1·429 mg.; therefore, 1 c.c. seminormal permanganate = 0·004 g. = 2·798 c.c. oxygen.
x = vol. NO, corresponding to the N_2O_3 present in the mixture.
y = " " " N_2O_4 " "
z = " " " HNO_3 " "

nitrogen acids to consist of N_2O_4, they are calculated as such; if more oxygen is present, the excess is calculated as HNO_3; if less oxygen is present, the excess is calculated as N_2O_3. In reality the ordinary nitrous vitriols do not contain any nitrogen peroxide, so that it is best to calculate the whole consumption of oxygen found by the permanganate titration as N_2O_3 or nitroso-sulphuric acid, and the remainder of the nitrogen as HNO_3.

In Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. p. 345, and in Lunge's *Technical Chemists' Handbook*, 2nd edition, p. 14, tables are given showing the amounts of milligrams of N, NO, N_2O_3, HNO_3, and $NaNO_3$ corresponding to 1 to 9 c.c. NO.

Analysis of mixtures of Sulphuric and Nitric Acid, as employed for nitrating processes, and in the *waste acids* from such processes.—Lunge and Berl (*Z. angew. Chem.*, 1905, p. 1681) perform this as follows:—

1. The total acidity is found by titrating 1 g., weighed off in a "bulb-tap pipette" (shown in Fig. 54, p. 360 of our text) with normal caustic-soda solution, employing methyl-orange as indicator, but adding this only at the close of the operation, or renewing it when destroyed. Or else the acids are sursaturated with a measured volume of soda solution, the methyl-orange is then added, and the retitration performed by normal acid.

2. The nitrous acid (or nitrogen peroxide) is found as described on p. 388, viz., running the mixed acids slowly into a measured volume of seminormal permanganate solution, of which 1 c.c. indicates 0·023005 g. N_2O_4.

3. The total nitrogen acids are found by means of the nitro-

nitrating processes and of waste acids is described by Finch in *Z. f. Schiess- u. Sprengstoffwesen*, 1912, p. 113; *Chem. Zentr.*, 1912, i. p. 1862. He adds to the acid mixture an excess of precipitated barium carbonate, boils for five minutes, washes the mixed precipitate of barium sulphate and carbonate, boils the filtrate with standard sodium carbonate solution, washes the precipitate formed up to neutral reaction, and retitrates the sodium carbonate still present. He thus finds the nitric acid, from which the nitrous acid found by the permanganate titration must be deducted. The amount of total nitrogen found by the nitrometer is rather higher than that found by the just-described method, which is probably owing to the presence of esters of glycerin-nitrates. Another process described *loc. cit.*, p. 388, is this: 10 g. of the acid mixture is diluted to 1 litre; 50 c.c. of the diluted acids are titrated with decinormal baryta solution, employing phenolphthalein as indicator; the solution is now boiled, filtered, and the filtrate titrated with a neutral solution of potassium chromate, K_2CrO_4. The end of the reaction is indicated by the yellow colour produced by an excess of potassium chromate. The $Ba(OH)_2$ consumed shows the total acidity, the K_2CrO_4 that due to NHO_3+HNO_2; the HNO_2 is found by titration with potassium permanganate. Any nitroglycerin present does not interfere with the process.

Corvazier (*Chem. Zentr.*, 1912, ii. p. 453) neutralises the acids exactly with barium hydrate, which precipitates barium sulphate and transforms the nitric acid into barium nitrite. Now decinormal soda solution is added, while observing the electric conductivity. At the moment when all the BaO of the barium nitrite is precipitated, and therefore free sodium carbonate is in solution, the electric conductivity shows an increase. This proceeding is declared to be accurate within 0·2 per cent.

off into another bottle, mixed with 2 g. dry calcium hydrate, and filtered. The refined and unrefined petroleum are then compared in a Krüss colorimeter. If the difference of colours is to be expressed in figures, the petroleum is best compared with a solution of potassium chromate. If the petroleum shows no discoloration, the sulphuric acid may be depended upon for refining it. Of its impurities, those which are injurious are the nitrogen oxides, which have a nitrating action, and selenious acid, which acts as an oxidiser. Even less than 0·01 per cent. of nitrogen oxides may produce a dirty colour; we must remember that commercial sulphuric acid contains 0·02 to 0·04 per cent. N_2O_3.

CHAPTER IV

THE PRODUCTION OF SULPHUR DIOXIDE

A. FROM BRIMSTONE.

Page 413. W. Feld has obtained for his brimstone-burner, mentioned in the text, the Ger. P. 262326. The sulphur is volatilised in a horizontal bottom chamber, where part of it is already burned; the vapours go into another, perpendicular chamber, placed above the bottom chamber, where they are burned. The top chamber is surrounded by a pipe; the air serving for the combustion of the sulphur passes through the concentric space thus formed, where it is preheated, and enters below into the chamber by a slot. In the centre of this chamber there is a perpendicular pipe for supplying the brimstone.

Whalen (U.S. P. 1065750) passes the gases from the sulphur-burners through a chamber provided with interchangeable partitions, where they meet air on a long way, so that any sulphur carried along is here burned.

The revolving sulphur-burner of Tromblee and Paull (supplied by the Glens Falls Machine Works, Glens Falls, New York) is recommended in advertisements of the technical journals as one of the best for this purpose. It furnishes gases containing up to 18 per cent. SO_2, requires but little space, and takes less than twenty minutes from starting till full working. A guarantee is given for each burner supplied.

Walther and Chemische Industrie- und Handelsgesellschaft, chamber, constructed with an outer metal casing and an inner lining of firebrick, provided with an outlet and with a number of superposed compartments (each with controlled air inlet) by a series of burner trays or dishes, the edges of which extend loosely between the lines of firebrick, spaced from the inner surface of the casing. The trays have semicircular lines of perforations near their edges, to allow the overflow of material to the trays beneath and the passage of combustion products. A receptacle for the supply of sulphur, having a conical bottom portion, with valved discharge opening, extends centrally into the upper part of the chamber, so as to receive heat from the combustion products, and discharges its contents into the uppermost tray. The discharge outlet of the chamber may communicate with a supplementary combustion chamber.

Coombs (U.S. P. 1147376) burns sulphur in a chamber containing a retort into which molten sulphur is run continuously; a jet nozzle, supplied with a regulated air-current, and in open communication with the retort and chamber, directs a flame jet on to the bottom of the retort.

Descamps (B. P. 100939 of 1916) describes a furnace for obtaining a mixture of SO_2 and N by means of dry air (*J. Soc. Chem. Ind.*, 1916, p. 963).

Lehmann (Ger. P. 291426) obtains SO_2 from burning brimstone mixed with sulphur ores.

Pagliani (*Ann. Chim. anal.*, 1915, p. 75; *J. Soc. Chem. Ind.*, 1915, p. 1050) states the maximum temperature attainable by the combustion of sulphur, required to yield burner-gases containing about 10 per cent. SO_2, =900°. The actual measurement of the temperature by means of a Le Chatelier thermocouple showed in the space above the burner-pan 340° ten minutes after charging, 370° after fifteen minutes, 420° after twenty-five minutes, and 495° after eighty-five minutes. The highest tem-

Unoxidised Sulphur.—The amount of residue being very small, it is quite possible to judge by mere inspection whether the combustion had been perfect or not. In doubtful cases a sample is tested for free sulphur by heating in a porcelain capsule, or by oxidation with aqua regia.

Treatment of the Gases from Brimstone-burners.

If these gases are to be employed for the production of calcium-bisulphite liquor for the manufacture of wood-pulp, they must be not merely cooled, but also purified from sulphur trioxide. Processes for this object have been mentioned in several places of our text in the description of modern sulphur-burners.

B. FROM PYRITES.

Page 418. *Mechanical stone-breakers* are described by P. H. Müller (Ger. P. 295170) and Polysius (Ger. P. 295035).

Page 441. A charging arrangement for pyrites-burners is described in the B. P. 2367 of 1912, and in the U.S. P. 1089304, of Battaille and Piperaut.

Buddeus (Ger. P. 285888) describes a kiln for roasting pyrites, in which the ore gets a preliminary roasting in an upper compartment, and descends through a grating, capable of being closed, to the lower compartment, where air is introduced under pressure.

Page 445. The scientific principles of roasting processes are treated by Schenk (*Z. angew. Chem.*, 1913, p. 641), especially also with respect of the roasting of ores containing less sulphur than iron pyrites, such as copper pyrites and blende.

Keppeler (*Chem. Zeit.*, 1913, p. 1219) made comparative trials on the burning of Norwegian and Spanish pyrites. Putting the same duty on a set of kilns, less sulphur was burnt facture of sulphuric acid as being inferior to that of Spanish pyrites. He had distinctly stated that his figures possessed absolute validity only for the special construction of the burners employed by him, and that his results were not to be extended to other descriptions of the Norwegian and Spanish ores than those employed by himself. Every practical man knows that every kind of ore makes special claims on the burners with respect to the amount of ore got through, the way of the ore, the intensity of the stirring operation, etc. His own experiments had been carried through three days, of which Uhlmann selected only one day for making his conclusions. In Uhlmann's own trials Norwegian pyrites was roasted off very well in a three-stage burner, but he had made no comparative trials with Spanish ore. [We must also point out that both Keppeler and Uhlmann made their trials with pyrites-smalls, and that their results cannot be accepted as being equally valid for ore in lumps.—G. L.]

Page 445. Channing (Ger. P. 250772) roasts pyrites in such a way that, apart from gases suitable for the manufacture of sulphuric acid, a residue (cinders) is obtained fit for the manufacture of iron. For this purpose he carries on the process in such manner that the sulphur goes away as SO_2, together with an excess of oxygen, and that all the iron present is converted into ferric oxide.

Debuch (Ger. P. 269774) carries out the burning of pyrites completely, in such manner that the metals present, apart from the iron, viz., copper, zinc, and lead, are completely converted into sulphates. Since this, especially in the case of cupric sulphate, takes place at 600° to 650°, this temperature is attained by transferring part of the ore from the first to the third, from the second to the fourth burner, and so forth, with the result that in none of the burners is there such an fresh ore is charged into the annular space thus formed. In order to prevent any sintering of the charge, by the temperature rising too high, steam is blown in along with the air.

The Nichols Copper Co. (Ger. P. 288013) provides, apart from the outside charging arrangement, an inside charger, consisting of a funnel and a periodically moved scraper.

Fusina (Ger. P. 288477) roasts sulphur ores by passing in the air in turns in one or in the opposite direction. For this purpose he employs a chain-grate, which passes through bells arranged above and below the grate in such manner that the air is drawn off in turns above and below; or else a furnace with a fixed grate, provided with a movable hood, connected to an exhauster by openings above and below.

Page 445. *Testing of Pyrites Cinders (Burnt Ore) for Sulphur.*—This can be done, of course, by the wet methods described in the text, pp. 95 *et seq.* But at the factories these methods are only exceptionally employed, because they are even more troublesome and lengthy for testing burnt ore than for fresh pyrites, and because dry methods exist which are both rapid and sufficiently accurate. Indeed, Jene (*Chem. Zeit.*, 1905, p. 362) maintains that the wet methods are altogether unsuitable for testing pyrites cinders intended for being worked up in blast-furnaces, as they do not give the total, but only the "available" sulphur; and this has been confirmed by Gottlieb (*ibid.*, 1905, p. 688). Jene also estimates the sulphur of the sulphates, soluble in water; so does Mennicke (*ibid.*, p. 495).

Not all the dry methods are sufficiently accurate or convenient for the daily use at vitriol works. This holds good, for instance, of the methods of Pelouze and of Kolb (p. 103 of our text). More suitable are the methods now to be described.

Böckmann proceeds as follows. A sample of the burnt ore is taken every twelve hours, every kiln being provided with by quartering on a piece of stout paper, and one of the quarters is finely ground and sieved. Finally, several grammes of every sample are ground in successive small portions in an agate mortar until no grittiness is felt on rubbing between the fingers; 1·5 to 2·0 g. of the very finely ground material are weighed off, and mixed with about 25 g. of a mixture of 6 parts sodium carbonate and 1 part potassium chlorate; this mixing is done in a large platinum dish by the aid of an agate pestle fixed to a wooden handle. The mixture is then fused over the blowpipe. The melt is allowed to cool till only just luke-warm, then covered with hot water, heated to boiling, and both this solution and the insoluble residue are washed into a 250 c.c. flask. The contents are cooled under a water-tap, made up to the 250 c.c. mark, and four-fifths of the solution filtered through a pleated filter paper into a 200 c.c. flask. The insoluble portion of the melt (oxides of iron, copper, etc.) only occupies a small volume; it is acidulated with hydrochloric acid, and the sulphuric acid estimated in the usual manner.

The method of Watson, described in the text, p. 104, is much more rapid than that of Böckmann, and the drawbacks connected with it in its original form have been removed by the modifications of Lunge (*ibid.*); but in the case of ores containing much zinc, or in that of zinc-free cinders containing 6 per cent. or upwards of sulphur, the following mixture must be substituted for that given in the text, in order to ensure complete oxidation and to guard against fusion: 1·6035 g. of the sample, 2·000 g. sodium bicarbonate, 4 g. potassium chlorate, and 2 to 3 g. ferric oxide, free from sulphur. The determination is otherwise conducted as described in the text (Lunge, *Z. angew. Chem.*, 1906, p. 27).

The following process is employed in one of the largest French works for the regular daily control of the working of by non-vulcanised rubber stoppers carrying glass tubes, are arranged in a furnace heated by a six-flamed Bunsen burner. The glass tubes are connected at the inlet end with a hydrogen generator by means of a corresponding number of lengths of rubber tubing furnished with screw clips; the outlet pieces are connected with vertically bent tubes which dip into small test-glasses. The hydrogen used must be freed from any accompanying hydrogen sulphide by washing with silver nitrate solution. Each set is numbered, and the porcelain tubes, stoppers, inlet- and outlet-tubes and test-glasses are marked to correspond. A preliminary test is first made to ensure that no precipitate results when the hydrogen is passed into the silver nitrate solution in the test-glasses. When this has been ascertained, exactly 1 g. of the finely ground cinders is weighed into a numbered porcelain boat, the boat pushed to the marked position in the porcelain tube by means of a glass rod, and 25 c.c. of silver nitrate solution (containing 10·604 g. $AgNO_3$, corresponding to 3·65 g. NaCl, per litre) is placed in each test-glass. When all the weighed samples are in position, a current of hydrogen is passed through the tubes, and regulated by means of the screw clips to two or three bubbles per minute. After ten minutes, when all the air has been expelled, the furnace is heated, at first gently, and then gradually raised to a red heat. After one and a half hours' heating the elimination of the sulphur is complete. This is shown by no further cloudiness appearing in the silver nitrate solution, and by the improved and satisfactory settling out of the black precipitate of silver sulphide. The gas supply to the furnace is then gradually reduced, and the hydrogen current interrupted. The test-glasses are removed in turn, and without filtering off the precipitate 1 c.c. of iron-indicator (2·5 g. ferric nitrate dissolved in 100 c.c. nitric acid of sp. gr. 1·38) is added, and

Abstr., 1916, ii. p. 263) transfers 1·3738 g. of cinder, ground to pass 100 mesh, to a 50 c.c. wrought-iron crucible containing 7 g. powdered sodium peroxide, mixes well up, sprinkles a little peroxide over the surface, covers the crucible, and heats over a moderate flame until the contents are in quiet fusion. After cooling, rinse the crucible cover into a 400-c.c. beaker, and add water to make up to about 50 c.c. Dip the crucible into the water, letting it rest on its side, and cover the beaker by a watch-glass; when the action is over, remove and rinse the crucible, add hydrochloric acid slowly until the iron residue is dissolved, avoiding any great excess of acid, and transfer to a 500-c.c. flask. Add 0·4 to 0·5 g. aluminium powder, shake well until the iron is reduced, heat to boiling until the aluminium is nearly all dissolved. After cooling, make up to the mark, pass through a dry filter, pipette 200 c.c. into a beaker, dilute to 450 c.c., add 1 c.c. concentrated hydrochloric acid, precipitate by 25 c.c. of a 5-per-cent. $BaCl_2$ solution, filter through a Gooch crucible packed with asbestos, and dry this in a flame. The $BaSO_4 \times \frac{100}{4}$ gives the percentage of sulphur.

The method employed by the General Chemical Company, New York (*Z. anal. Chem.*, 1911, p. 187) has been modified by Sznajder (*Chem. Zeit.*, 1913, p. 1107) as follows:—2·5 g. burnt ore, finely ground, is mixed with 1 g. anhydrous sodium carbonate and 4 g. zinc oxide, and heated for half an hour to red heat in an open, inclined iron crucible (40 mm. high, 50 mm. wide at the top, and 30 mm. at the bottom), now and then stirring the contents. After cooling, the mass is taken up with boiling water, washed into a 250-c.c. flask, filled up to the mark, 200 c.c. filtered off, heated to boiling, phenolphthalein added, then dilute hydrochloric acid up to decolorisation, then 30 c.c. one-fifth normal barium chloride

Martin (*Monit. Scient.*, 1913, p. 687, and 1914, p. 86) treats 3 g. finely ground pyrites cinders with aqua regia, takes up the residue with hydrochloric acid, dilutes with warm water to about 100 c.c., precipitates the iron with sodium carbonate (of which about 8 g. is required), filters, washes, and titrates the solution. He describes a number of precautions to be taken.

Somerville (*J. Gas Lighting*, 1914, p. 241) burns the sulphur in the cinders by a current of oxygen, absorbs the gases in alkali, oxidises the sulphite by hydrogen peroxide to sulphate, and estimates this either by retitration of the alkali or by barium chloride.

The glass-instrument factory of Christ. Kob & Co. at Stützerbach, in Thuringia, recommends for the testing of sulphur in pyrites cinders an apparatus in which the tube for supplying the air is not fused to the flask, but carried through the cooler.

Page 445. *Estimation of Copper in Burnt Pyrites.*—Koelsch (*Chem. Zeit.*, 1913, p. 753) reduces the difficultly soluble ferric sesquioxide to protoxide by heating 10 g. of the burnt ore with 5 to 7 g. solid sodium hypophosphite and 40 c.c. hydrochloric acid (sp. gr. 1·16) to boiling, dilutes (without filtration) with 100 c.c. hot water, precipitates the copper by sodium sulphide solution, filters, ignites, adds a little nitric acid and sulphuric acid, drives the acids off by heating, and estimates the copper by electrolysis. For less accurate work, the filter and precipitate are heated with 10 c.c. nitric acid (sp. gr. 1·4), a little urea is added, the solution is cooled, rendered faintly ammoniacal, then acidified with acetic acid and titrated with thiosulphate, after adding potassium iodide. The treatment with hypophosphite and hydrochloric acid can be applied wherever highly ignited ferric oxide is to be brought into solution.

Estimation of Iron.—The ferric oxide of 0·5 g. pyrites cinders is dissolved by heating the burnt ore for some time with permanganate solution, of which every cubic centimetre indicates 0·005585 g., or, when working on 0·5 g. cinders, 1·117 per cent. iron.

Burning Pyrites-Smalls.

Page 459. Polysius (Ger. P. 262241) moulds small ores into balls by means of a special drum placed in front of the roasting-drum.

A. G. Anderson (Fr. P. 458442; Belg. P. 256447) moulds small ores ground down to 1 mm. in the moist state in revolving cylinders into porous balls, passing hot gases through the mass.

Gröndal (Ger. P. 277895) employs a tunnel-shaped furnace with flues in the walls, arranged lengthway, connected with a supply of air at the discharging-end of the furnace, and possessing in several places inside the furnace openings provided with regulators; if necessary, also with flues near the outlet, connected with a gas-generator and with a chimney. Porous ore-balls are easily permeable for gas. There is no formation of dust, which is a great advantage over the ordinary burners for smalls, and even over lump-burners, and allows of dispensing with dust chambers. The burnt ore is obtained in a very easily managed form, and can be immediately utilised for the production of iron. If necessary, it can be further treated in an ordinary burner for smalls.

Buddaeus (U.S. P. 1079897) burns small ore containing less than 30 per cent. sulphur, without any supply of heat from without, in kilns provided with a porous bottom through which air is blown in.

G. H. Benjamin (Ger. P. 274663) provides the shelf-burners with electrodes, in order to produce a higher temperature.

Brackelsberg (*Z. angew. Chem.*, 1916, 1, pp. 281 *et seq.*) describes the preparation of "agglomerated" balls of pyrites

31732, Austr. P. 15530; Hung. P. 28500; Russ. P. 9798; Swed. P. 17274; Norw. P. 13137.

Improvements are described in B. Ps. 22022 of 1910 and 6372 of 1912; U.S. Ps. 1066110, 1123965, 1123966.

The Ger. P. 276570 of the Nichols Chemical Co. describes a burner with inwardly cooled stirring-blades, attached to a vertical hollow shaft, and provided with junctions protected against the heat of the furnace.

Page 497. *The Wedge burners*, according to Ger. P. 255648 of U. Wedge, can be worked from beginning to end of the roasting in an uninterrupted way, by employing a mechanical burner with several shelves; the upper shelves perform the pre-roasting, and the lower ones finish the process, after mixing a reducing agent, such as coal, with the product.

L. D. Anderson (*Eng. and Min. J.*, 1914, p. 51) reports that the Wedge furnaces have given excellent results for roasting lead matte at Medvall, Utah. The same (*ibid.*, p. 258) reports that lead matte is successfully treated by this burner in several American works; also copper regulus, which is roasted down from 22 to 5 per cent. sulphur. New American patents for these furnaces are U.S. Ps. 1123965 and 1123966.

Page 494. Truchot (*Rev. gén. chim. pure appl.*, 1914, p. 169) states that the furnaces of the Erzröstgesellschaft Cöln are an essential improvement over the original Kauffmann burner; they save 28 per cent. of space and 50 per cent. of power, and do 10 per cent. more work. In this type the revolving axis and the stirring-blades are cooled by air blown in by a fan-blast. The ore slides from one shelf to another by laterally inclined cast-iron plates, which greatly reduce the production of dust. The teeth of the stirring-blades are exchange-piece which passes through the inner wall of the shaft by a slit, and on the turning of the shaft by 90° lays itself against the inner side of the shaft. At the other end of the rod there is an enlargement which, on the progress of the rod, places itself firmly against the fore-end of the stirring-blade, and thereby presses this blade against its bearings on the shaft. The front end of the rod may be provided with a screw-thread, the nut of which is sunk in the stirring-blade, which presses against a projection provided in the inside of the rod, and thereby fastens the blade. The advantage of this arrangement consists in the secure and gas-tight attachment of the stirring-blades on the shaft, without employment of any fastenings liable to be burnt. Ger. P. 268602 of the same firm describes a short bolt, in lieu of the rod, pressing by means of a nut against a projection at the back-end of the blade. This avoids any arrangement which easily burns fast by the action of the heat, the roasting-gases, and the dust. Further modifications are described in their Ger. Ps. 273942, 288405, and appl. M50050 and M55925.

John Harris (B. Ps. 23331 of 1910, 28078 of 1911, 21897 of 1913; Ger. Ps. 247695 and 259208; Fr. P. 432121) describes a mechanical burner, divided into vertical compartments, with arrangements at the flues and slides permitting repairs. The lower coils are placed in a cooling channel. Above the arched bottom of the lowest roasting-bed there is a partition with zig-zag channels for introducing heat from without for the purpose of completing the roasting. The ore is supplied in successive portions; every charge is removed from the neighbourhood of the entrance plane previously to the arrival of the next charge, and the ore is moved over the furnace bed in such a way that every charge is kept separated from those preceding and following it, up to the time that it has approximately attained the proper temperature. According to *Chem. Trade J.*, 1914, p.

chamber required, and the gas can be passed from the gas flue straight into the Glover tower. For each compartment one horse-power is required to do the work. The Harris Furnace Company at Sheffield contends that their furnace is cheaper than all other mechanical burners, and equally well adapted for rich and small ores; for the roasting of zinc-blende and other sulphides it may be provided with an auxiliary heating arrangement.

The same inventor (Ger. P. 273045) describes an agitating-shaft for mechanical ore-burners, provided with water- and air-cooling, with water-cooled, rake-shaped stirring-blades for the higher outside compartments, and air-cooled blades for the central, lower compartments, which travel mostly within the roasting material; this admits of greatly reducing the height of these central compartments and of working economically.

Düron (Ger. P. 275751) describes special shapes of stirring-blades. The same (Ger. P. appl. D28657) describes a charging apparatus for mechanical burners, allowing of very exact regulation, consisting of a helix causing a continuous agitation, avoiding any intermediate machinery (such as levers, toothed wheels, ropes, etc.), and loosening and drying the material, without requiring any supervision.

Martin (Ger. P. 272918) prepares finely ground sulphide ores for the wet concentration by roasting to a moderate extent, with addition of a fixed or liquid oxidising agent. The iron pyrites is first oxidised; the mass may then be subjected to a concentration by water, in order to separate the ferric oxide formed from the sulphides of lead and zinc, and these mixed sulphides may be again subjected to a moderated roasting process, in order to oxidise the zinc sulphide. By a second concentration, the zinc oxide and sulphate (if such is present) are separated from the lead sulphide.

the ore in a direction perpendicular to the motion of the stirrers by moving these backwards and forwards. At one or several rods, arranged transversely to the longitudinal axis of the furnace, rods are placed which are made to travel backwards and forwards; to them a number of stirring-blades is attached moving in the longitudinal direction, with V-shaped or ploughshare-like stirrers. The patent specification describes a number of ways of carrying out this system. These burners, which are working at the zinc works at Neuss, are reported to work very well. Hommel's Ger. P. 292487 describes various forms of stirring-blades for mechanical roasters.

The mechanical dust-burners of Bracq and Moritz (*not* "Bragg," as spelt on p. 501, line 19) is described in detail by Barth in *Chemische Apparatur*, 1915, pp. 95 and 105. According to *Chem. Zeit.*, 1914, p. 816, forty such burners had been built during the last four years. According to *Chem. Zeit. Rep.*, 1914, p. 336, this burner roasts the sulphur in pyrites from 50 per cent. down to less than 1 per cent.; each burner requires 0·1 to 0·25 h.p. The cinders in the bottom compartments are nearly cold, which in the case of cupriferous ores greatly facilitates the extraction of the copper.

Barth (Ger. Ps. 289259 and 291886) describes a mechanical dust-burner containing a number of hearths, which are in turns fixed and moving; they revolve on a common hollow axis, consisting of two concentric tubes, one of which serves for introducing cold air into the single compartments, the other for taking the heated air away.

Page 501. *Various Mechanical Burners for Pyrites-Smalls.*—The Ger. P. of the Metallbank und Metallurgische Gesellschaft is No. 243913, that of the Maschinenbauanstalt Humboldt, No. 243613. Other patents:—Société minière et métallurgique de Peñarroyna (Ger. P. 275908); Bracq (Ger. Ps.

and 15463 of 1914); Parent (Ger. P. 264709); Wocke (Ger. P. 216657); Fowler (B. P. 7471 of 1914); Claude (Fr. P. 468968); Renwick (Ger. P. 246180); Herzig (U.S. P. 1108906); Timm (Austr. P. appl. 9226 of 1913); Ramén and Beskow (B. P. 12214 of 1911; Ger. P. 253320); Edwards (Ger. Ps. 242888, 250774, and 255747); Ernest (Austr. P. appl. 2496); Chemische Industrie Akt. Ges. and Singer (Ger. P. 262610); S. et G. Dumont et Frères (Ger. P. 262183); Bousse (Ger. P. 280523); W. A. Hall (B. P. 20759 of 1912; U.S. P. 1076763); Ridge (B. P. 23763 of 1912); Zetsche (Ger. P. 280430); Saccharinfabrik A. G. vorm. Fahlberg, List & Co. (Ger. P. 257537); Zavelberg (U.S. P. 1107006; Fr. P. 468685; Ger. Ps. 284607 and 292809); Sarrasin (B. P. 26915 of 1913; Fr. P. 451182); Aktiengesellschaft für Zinkindustrie vorm. W. Grillo and Schefczik (Ger. Ps. 280427 and 280429); Selas (Ger. P. 285913); Lütgens and Ludewich (Ger. P. 262128; Fr. P. 449144; U.S. P. 1176070); Nichols Copper Company (Ger. Ps. 276570, 284586, 286381, 287079, 288013, 289998, and appl. No. 15180); Nichols Copper Company and Stout (B. P. 9958 of 1915); Hildebrandt (Ger. P. 290733); Maschinenfabrik A. G. vorm. Wagner & Co. (Ger. Ps 290534 and 291239); Jenks (U.S. P. 1179928); Mount (U.S. P. 1179952); de Spirlet (Ger. P. 292371); Hommel (Ger. P. 292794).

Keppeler (*Chem. Zeit.*, 1913, p. 1220) makes critical remarks on the modern burners for pyrites-smalls. He points out that many so-called improvements have not stood the trial of practical experience. Thus, *e.g.*, the shortening of the way which the ore has to travel by increasing the stirring-up of the material, whereby the velocity of the roasting process is increased, has the drawback that it is less easy to adapt one's self to changes in the conditions of working. More success for

C. ROASTING OF ZINC-BLENDE.

Page 501. *Purification of Zinc-blende by Washing.*—Emerson (U.S. P. 1126965) separates blende from impurities by carrying the powdered ore in a thin layer through a bath which acts upon the blende, with formation of gas, just up to the point that the particles of ore are lifted by the adhering gas a little above the surface of the layer, and can be mechanically removed from the mass below by a revolving set of cups. The bath serving for this purpose may be dilute (10 per cent.) sulphuric, hydrochloric, or nitric acid, or a solution of sodium chloride or sulphate in which by electrolysis acid or chlorine is liberated.

Page 507. *Various Processes.*—Hommel (Swiss P. 72083) describes a special construction of a muffle for roasting blende. Queneau (U.S. P. 1132684; Fr. P. 445233; Ger. P. 288648; B. P. 15460 of 1912) roasts blende in an electrical furnace.

Borchers, Schenk, and Thomas (Ger. P. 242312) convert the blende into briquettes, and roast these at a temperature of 700° to 800° on movable grates in the flame of a furnace working with a flame containing an excess of oxygen and aqueous vapour. In this case it is stated that no zinc is volatilised, nor is there any zinc sulphate formed.

Buddaeus (B. P. 29042, 1913; Ger. P. 278443; Fr. P. 466397) converts the blende into briquettes, applying calcium silicate as a cementing material, in case of necessity with addition of a combustible substance. Owing to the porosity of these briquettes the sulphur can be roasted off without fuel till below 1 or 2 per cent. His U.S. Ps. are 1079897 and 1121226.

Saulles (U.S. P. 1183172) roasts blende (with the addition of carbon near the end of the roasting) with a regulated other. The top drum is sufficiently heated by the hot gases evolved in the bottom drum. The blende, after receiving a first roasting in the top drum, falls into the bottom drum, where it receives its final roasting; in that drum hot-air pipes are arranged, heated by producer-gases. The heating-gases are kept separated from the roasting-gases.

Zelewski (Ger. P. 195724) employs two muffles, both of them with stirring apparatus, independent of each other, and capable of being worked in opposite directions. If the blende is not sufficiently roasted off, the stirring apparatus of the top muffle is stopped, and the blende moved backwards and forwards in the bottom muffle until it is sufficiently desulphurised. As the stoppage of the top muffle causes a great diminution of the ore got through, and in case of blende inclined to fusing may lead to awkward disturbances, the inventor, at Hommel's advice, took the Ger. P. 201191, according to which a continuously working furnace for the first roasting is combined with two or more furnaces in which the ore can be kept as long as it is necessary to complete the roasting.

Hommel states that the blende-roasting furnaces provided with inside stirrers are by far inferior to the revolving-hearth furnaces, both with respect of the cost of plant and repairs, and of their reliability. The revolving-hearth furnaces have no parts moving in the hot gases, and their stirrers require no cooling, but consist of plain, flat steel, easily replaceable. Repairs at the muffles of the MacDougall kind (p. 474 of our text) are very difficult to make, whilst they are easily made at hearth furnaces. The MacDougall furnace requires less ground space, but is very much higher (a furnace for getting through 15 to 20 tons is about 33 ft. high), which causes extra expenses for stairs and platforms, and greatly interferes with the control of the single muffles. That furnace also produces very much dust, as the gases on ascending strike against the ore falling

Figs. 6 to 8. According to epistolary information from that firm, this furnace possesses a great many advantages. It has been possible to roast in it blende containing 37 per cent. zinc, 13 to 19 per cent. iron, and 3 per cent. lead, down to 0·7 per cent. sulphur, and even damp ore can be worked with it by providing a mechanical drying stove on the top of the furnace. According to Hommel, this furnace admits of a much more thorough turning-over of the ore than any other, which is caused by the fact that the ore does not merely progress in a given direction, but is strongly stirred up, especially in the mixing-zones, without being moved forward for a great length. Especially in this respect the Merton furnace has a great advantage over the Hegeler furnace, in which the ore is turned over at most once every one and a half hours. A 12½-ton Merton furnace has about the same dimensions as a Hasenclever furnace block. Three muffles are superposed over one another; only the bottom muffle is heated from below and above by producer-gas. There are six perpendicular shafts, provided with stirring-arms, and cooled by water. The two outside stirrers make the ore travel steadily forwards; the four inside stirrers are arranged in pairs, and thus produce two mixing-zones in which the ore is most energetically treated. Heated air is passed into the bottom muffle, which produces a complete roasting-off of the blende. At full work each furnace requires 6 h.p.; one man can attend to four furnaces. The cost is £1500 all complete Hommel considers this furnace to be far better for roasting blende than any other. The muffles of the Merton furnace are comparatively low, which is produced by placing the leading-point of the stirrers at the highest point of the muffle. The only drawback which might be urged against this furnace is that in certain places not touched by the revolutions of the stirrers, dead

FIG. 6.

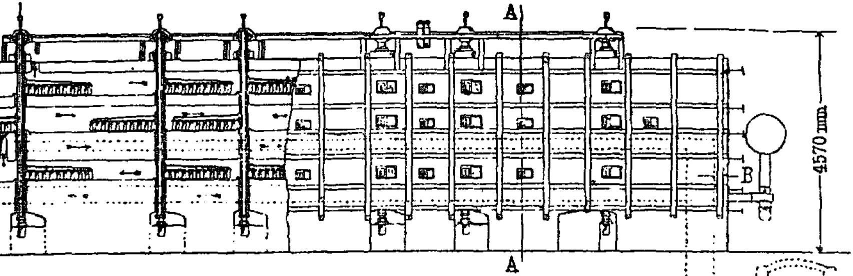
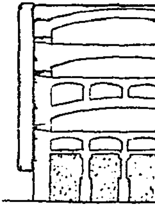


FIG. 7.



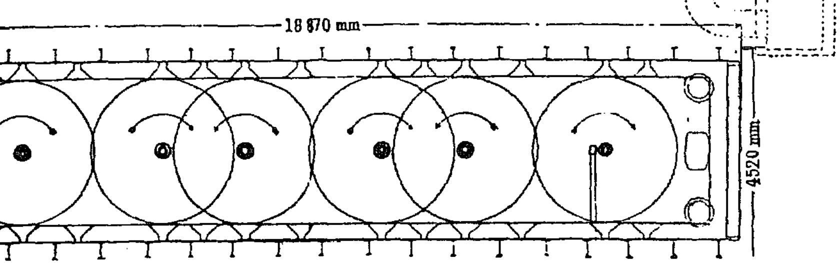


FIG. 8.

Vivian (*Z. angew. Chem.*, 1915, ii. p. [illegible] this furnace.

Spirlet's furnace (*Eng. and Min. J.*, xcviii. p. 617; Ger. Ps. 236089 and 292371) consists of three circular hearths turning round a central shaft, and a fixed hearth underneath. It roasts in twenty-four hours 5 tons blende, with less than 1 h.p. and a consumption of less than 10 cwt. coal. The roasting-gas contains from 5 to 7 per cent. SO_2. Australian blende can be roasted off to 1 per cent., Algerian blende to 2 per cent. sulphur in the cinders. The Spirlet furnace is working at the Vieille Montagne Co. at Overpelt and Engis in Belgium, and at Stolberg in Prussia; another furnace was being built in 1915 at one of the works of the Grasselli Chemical Co. in West Virginia. In comparison to the Hegeler furnace (pp. 498 and 1566), widely used in the United States, it has no advantage with respect of prime cost, but with that of the cost of working.

In *Eng. and Min. J.*, xcix. p. 420 (1915), the various types of blende-roasting furnaces working in the United States are enumerated. For the production of sulphuric acid the Hegeler furnace is exclusively employed, which, since its introduction in the year 1882, has not been materially changed.

Rissmann-Rübel's blende-roasting furnace (*ibid.*, p. 326) is a modified Zellweger furnace, 155 ft. long, consisting of two parallel hearths 8 ft. wide, between which the spindle of the stirrers is carried on a frame. The arch rests at the outside on brickwork, and is supported inside by an iron frame. A weak point is that the arrangement for keeping the slot in which the stirring arrangement is running is very imperfect.

Other patents for mechanical blende-roasting furnaces:—Dohet (Ger. P. 258261); Helsingsborgs Kopparwerks Aktiebolag (Ger. P. 261605); John Harris (B. Ps. 23331 of 1910 and 7722 of 1912); Kessler (Ger. P. 270273); Aktiengesellschaft für Zinkindustrie vormals Grillo and Schefczik (Ger. Ps. 280427, Lütgens (Ger. P. 260156); Nichols Copper Co. (Ger. P. 276570); Klepetko (Ger. P. 185013); Lütgens and Ludewich (Ger. P. 275464); F. D. Baker (Ger. P. 232895).

Max Liebig in his book, *Zink und Cadmium*, 1913, pp. 234 *et seq.*, describes a number of other furnaces for this object.

Page 511. *Comparison of the Various Blende-roasting Furnaces.*—We follow in the first instance the statements of Hommel (*Metallurgie*, 1912, pp. 294 *et seq.*). He gives the following data concerning several of the most important furnaces:—

	Hasenclever-Rhenania. Each hearth 90×4 feet.	Modified Malétra-Delplace.	Hegeler.	Merton.	Preliminary roasters.	
					4 shelves of 20 feet diameter.	Two MacDougalls, each with 6 shelves, 18 feet diameter.
Number of attendant men	8	8	12	4	4	4
Daily work, tons . .	7	10	40	50	60	30
Kilograms, per man .	875	1,250	3,333	12,500	15,000	7,500
,, per superficial metre of hearth.	54·7	100	65·8	80·5	300	200
Cost of plant . marks	20,000	20,000	250,000	4 × 30,000	4 × 25,000	2 × 70,000
,, per ton ,,	2,857	2,000	6,250	2,400	1,666	4,666
Coal consumed, per cent.	22	12	30	14	10	15
Power required, horse-power . . .	...	...	12	4 × 6	4 × 1	2 × 7
Hearth surface, superficial metres . .	128	100	608	590	200	150
Desulphurising factor per superficial metre of hearth superface .	1	1·8	1·2	1·5	5·5	3·6
Working cost per ton:—						
Wages . . marks	5·71	4·00	1·50	0·40	0·33	0·66
Coal . . ,,	2·20	1·20	3·00	1·40	1·00	1·50
Power . . ,,	...	...	0·72	1·15	0·16	1·12
Repairs . . ,,	0·30	0·30	1·00	0·70	0·50	0·80
Amortisation . ,,	0·78	0·55	1·70	0·66	0·46	1·28
Management, etc. ,,	1·00	1·00	1·00	1·00	1·00	1·00
Total cost per ton, marks	9·99	7·05	8·92	5·31	3·45	6·36

through dead-roasting furnaces and leaving it in these until the desired degree of desulphurisation has been attained.

All the statements of the table refer to a two-shift day of twenty-four hours. The following special remarks have to be made:—

Number of Attendant Men.—This is particularly high for the Hegeler furnace, owing to its mechanical imperfections. Owing to its great height, one man can attend only to two such furnaces, against four Merton and revolving-plate furnaces. Besides, one fireman is calculated for each set of furnaces.

Quantity of Ore got through per Day.—This is very high in case of the preliminary roasters, since the ore is not kept in them anything like as long time as in the dead-roasters.

Cost of Plant.—This is by far the highest for the Hegeler and MacDougall furnaces, and lowest for the Rhenania furnace. The best comparison is obtained from the cost of plant per ton of ore got through; this is much lower for the shelf-roasters and the Merton furnace than for the Rhenania furnace. The cost stated for the Hegeler furnace is rather below the fact.

Coal and Power.—The consumption of these is far the lowest for shelf-roasters; for the Merton furnace it is higher than for the Hegeler furnace, owing to the much more thorough working of the ore.

Desulphurising Factor.—This is comparatively low for the Hegeler and Merton furnaces. The factor of the Rhenania furnace is put = 1, as it is the lowest. This is an average, as the three muffles of that furnace have the comparative factors 1 : 2 : 4.

Working Cost.—For this the following rates were assumed, which of course are subject to great local variations:—

Daily wages . .	5·00 marks per shift.
Coal . .	10·00 ton

there is room for combining it with one or more dead-roasting furnace.

According to Hasenclever (*J. Soc. Chem. Ind.*, 1911, p. 1291), the progress in the development of mechanical blende-roasting in Germany during the year 1911 was but slow. Many spelter works had spent a good deal of money for experiments with blende-roasting furnaces of their own construction. The main difficulty is that the German spelter works are frequently compelled to use blende containing lead, which sinters during the roasting and adheres to the stirring arrangements.

Schütz, who describes the various apparatus for roasting blende (*Metallurgie*, 1911, pp. 637-645), also comes to the conclusion that up to that time none of the mechanical blende-roasting furnaces had had a full success, and that the mechanical roasting of blende was at that time still in the experimental stage, at least in Germany. In *Metall und Erz*, 1915, p. 109, he makes a report on the progress in the roasting of blende up to that time.

Page 511. *Results of the Roasting of Zinc-blende.*—According to H. O. Hoffman (*Trans. Amer. Inst. Min. Eng.*, 1904, p. 834), when roasting blende in the ordinary way, very little zinc sulphate remains in the cinders. To this Hommel (*loc. cit.*) remarks that Hoffman in his experiments had exceeded the temperature of decomposing the zinc sulphate. If the temperature is kept purposely low, 60 to 70 per cent. of the zinc contained in the blende may be obtained as sulphate. This sulphate begins to decompose soon over 600°, and is completely decomposed at 800°, at most at 850°. Therefore Hommel prescribes preheating the air before it enters into the bottom muffle. Mistakes in the way of heating cause the formation of matte and of ferrite in the cinders. A strong formation of zinc ferrite also takes place if blende containing much iron is heating from without or by the hot roasting-gases. 2. The ignited blende must be deprived of the greater part of its sulphur by thorough stirring and moderate supply of air, but without heating from without. 3. The nearly desulphurised blende must be brought into contact, at a temperature which need not exceed 800°, and with thorough stirring, with a strong current of air, but in such a way that it is not cooled thereby. 4. The space occupied by the ore in the muffle ought to be as nearly as possible equal to the free space. Hommel finds that most of the furnaces now used do not satisfy these prescriptions, more especially those built on the Hasenclever principle. Much better than these are the old Eichhorn-Liebig furnaces (our text, p. 504) in a slightly modified form; also the Delplace furnaces, which, however, have an unduly complicated firing arrangement. Modern roasting-furnaces ought to be in any case worked with producer-gas.

Max Liebig treats of the same matter in his *Zink und Cadmium*, 1913, pp. 222 *et seq.*

Reed (U.S. P. 1069178) mixes the blende with part of the cinders from a previous operation.

Titus and Barenscheer (U.S. P. 1069498) mix blende with sodium chloride, heat it, and treat the cinders with chlorine.

The Ger. P. 272918 of Martin (*vide suprà*, p. 169) also belongs to this domain.

Mostowitch (*Z. angew. Chem.*, 1911, p. 763) describes the behaviour of zinc sulphate at high temperatures. He knows of cases where the sellers of roasted blende have been obliged to allow deductions from the selling price, owing to bad roasting.

Nemes (*Metallurgie*, 1912, p. 516; *Z. angew. Chem.*, 1913, ii. p. 55) writes on the roasting of blende in shelf furnaces. According to him, the decomposition of the sulphate is not merely depending upon the temperature, which is nearly identical with various samples of blende in the same furnace been almost entirely replaced in Belgium by the Delplace furnace (see below), which yields in twenty-four hours from 12 to 18 tons of cinders, with an expenditure of 10 to 12 per cent. of coal, which cost about 50,000 francs.

Maurice de Lummen (*Chem. Trade J.*, 1916, lviii. 255 and lix., p. 261) states that in Europe the Hasenclever (p. 504) and the Delplace furnaces, both of them muffle furnaces worked by hand, are almost exclusively employed for the roasting of blende; in the United States the Hegeler mechanical furnace (p. 508) is in general use. He finds great fault with the Hasenclever (Rhenania) furnace; according to him it is difficult to work, and the output of the operation is too small (800 or 900 kg. blende per diem); the roasting compartments are too tall, causing a bad use of the air and the production of gases poor in SO_2; the working doors are too large, and thereby allow the entrance of an excess of cold air, also hindering the frequent raking of the blende by reason of its rapid cooling; and the consumption of fuel is very high. Very much superior to the Hasenclever furnace, according to Lummen, is the *Delplace furnace.* This is composed of a series of units similar to those of the Malétra furnace (p. 465), and it is furnished with grates heating the lower shelf of each unit, the flames from the grates circulating under the lower shelf. The working of the furnace is the same as that of an ordinary Malétra furnace, the raw blende being charged on to the upper stage, and remaining a certain number of hours on each of the stages from top to bottom. A battery of Delplace furnaces is generally composed of nine, twelve, or fifteen units, each burning about 1 ton of blende per twenty-four hours. Every group of three units is furnished with two fireplaces, each of which has a muffle, heated by the heat radiated from the fire, and into which the coal is charged. In this muffle the coal distils, giving up its volatile matter and forming coke. When the evolution of volatile the burners, together with the recovery of the waste heat, enables the blende to be roasted with an extremely reduced quantity of fuel; several works employing this furnace have a consumption of fuel of 10 per cent. of the weight of the raw blende charged. The height of the roasting compartments of the furnaces (that is to say, the distance between the upper side of one slab and the lower side of the following one) is 6½ feet. The operating doors on each shelf are very small, and exactly proportioned to enable the introduction of the shaft of a rake, the section of which is about 12 in. to 1½ in. All this results in a great concentration of heat as well as a good utilisation of the air in the furnace. Sulphurous gases are obtained containing on an average 6·5 to 7 per cent. of SO_2. This is impossible to attain with any other type of blende furnace. The fact that the operating doors are very small, permits of working the furnace without its cooling in a sensible manner. The operation is the same as with a Malétra furnace. Each unit is worked with four or six hours' interval. The workman commences by emptying the lower floor containing blende completely roasted, then bringing down successively the contents of the furnace. When the uppermost floor has been emptied, he charges it with from 180 to 250 lb. of raw blende. Every hour or every two hours during the four or six hours' interval between the working of a unit, the operator rakes each floor of the unit so as to stir the blende and renew the layer on top. He thus works in a compartment of restricted dimensions, and has only to stir a minimum quantity of blende; he gets through 1000 to 1200 kg. Every time the furnace is operated to lower the blende from one floor to another, the ore is vigorously stirred and brought into contact with the air. The furnaces being back to back, each compartment is always worked at the same time as the corresponding compartment on the opposite side. The blende which

(3) Small operating doors, enabling of frequent stirring without cooling the furnace.

(4) Heating of the air introduced into the furnace.

(5) Low fuel consumption.

Of the *Hegeler furnace*, Lummen gives the following account. This mechanical furnace is employed in the United States by all the zinc works which transform the SO_2 gases produced in roasting blende into sulphuric acid. Introduced in 1882, it has scarcely been modified since. The furnace has two compartments, about 75 ft. long. Each compartment has seven shelves, the two lowest being fitted with muffles for the purpose of heating. The movement of the blende across the furnace is carried out by means of rabble arms dragged by a chain. The rake enters at one end of a shelf and leaves at the opposite end; then, after being cooled, it enters the furnace again. Every shelf is fitted at its two extremities with movable doors, permitting the entry and exit of the rakes. The height of the shelves is relatively great (about 2 ft.), which causes a deficiency in the use of the air and produces gases very poor in SO_2 (3 to 4½ per cent.). The blende is stirred at intervals varying from one and a half to two hours, which is little for a mechanical furnace. The capacity of a Hegeler furnace is about 40 tons of blende per twenty-four hours; and although the furnace is mechanical, the number of workers varies from thirteen to fifteen. The consumption of coal is very high, viz., 25 per cent. of the weight of the raw ore charged. The necessary power is about 40 h.p. In view of its dimensions, a Hegeler furnace cannot be constructed in an existing building. Considering that the price of the furnace is about $60,000, it is apparent that although the use of this apparatus is possible in America, it will not be so in Europe. Besides the disadvantages of getting an imperfectly roasted ore, and gases very poor in of the MacDougall type (*vide* our text, p. 474), trials which have established that this kind of furnace is not suitable. If built with a diameter only at the best great enough for obtaining a suitable production, the height of the roasting compartments becomes too great for a good utilisation of the air. Moreover, if the diameter of the furnace did not already require a considerable height of the arches, it would be necessary to construct it with a sensible distance between two consecutive arches, in order to replace, if required, a broken arm. Another disadvantage of the MacDougall type of furnaces is that they generally produce much dust. If this is not of capital importance in roasting pyrites, it becomes so in roasting blende, having regard to the value of the zinc. In addition, any furnace employing cast-iron rabble arms must have them strongly cooled with either air or water circulation. This, then, involves on the one hand carrying off the heat units from the furnace, whilst on the other supplying them by burning coal in' the fires. The only mechanical furnace tried in late years, and not having these inconveniences, is that invented by a Belgian engineer, *X. de Spirlet* (comp. our text, p. 509). The principle of the furnace is original, and entirely distinct from what has previously been tried. The characteristic of the apparatus is that it has no metallic parts in the interior of the furnace. This is composed of a certain number of platforms of fireclay material, superposed and alternatively fixed and movable. The fixed ones are carried on six columns arranged round the furnace, the movable ones turning about an imaginary vertical axis. They are fitted with rollers, and move on a rail carried by columns. Into the interior face of each arch are built a certain number of fireclay bricks arranged like teeth, and displacing the blende towards either the interior or the exterior. The space between two consecutive plates forms a shelf of the furnace, and is closed by a sand joint. Generally the furnace comprises three of the furnace when the number broken become too great. Several attempts have been made to roast blende in revolving drums like modern cement kilns. These attempts have never brought anything but disappointment to those who have made them. Besides the great difficulty of constructing muffle furnaces of that kind, the utilisation of the air is as bad as possible, giving gases containing a very feeble percentage of SO_2. Moreover, the roasting is defective. As far as Europe is concerned, one can say that up to the present no mechanical furnace has been definitely adopted for the roasting of blende. The utilisation of the gases from the roasting of blende, and the method of transforming them into sulphuric acid, are the same as for the gases produced by the roasting of pyrites. As the SO_2 contents of the gases from blende furnaces is not always so high as that of pyrites gases, for the same acid output a somewhat larger chamber space must be provided if blende is burnt. As most blendes contain fluorides, the life of the Glovers is generally quite short enough, whatever the quality of the packing employed. Usually after twelve or eighteen months' working the packing of the Glover must be replaced, so that one Glover must always be kept in reserve. The consumption of nitrate is practically the same as with pyrites, excepting always if furnaces giving gases poor in SO_2 are employed. As regards the life of the lead chambers, this is practically the same as with pyrites. Many continental and American zinc works employ the contact process in connection with their blende furnaces, the system most in favour seeming to be that of Grillo-Schroeder. It was at the zinc works of Grillo that Dr Schroeder invented and tried his contact process. The operation is not more difficult than with pyrites, except that more precautions must be taken in washing the gases before putting them in contact with the platinum, on account acid was made from blende, explainable by the fact that Belgium produced annually nearly 200,000 tons of zinc, representing a quantity of blende to be desulphurised of about 450,000 tons. So considerable a production would be possible only with difficulty, if the Belgian zinc works were obliged themselves to desulphurise all the blende treated in the zinc furnaces. That is why these factories have working arrangements with the acid works, more or less in their vicinity. The latter receive the raw blende, extract the sulphur, and then return the roasted blende to the zinc works. The roasting works receive the sulphur gratuitously, and also what is called a "roasting bounty"—that is to say, for each ton of blende roasted they receive a fixed sum, which ten years ago reached 10 or 12 francs. In later years this bonus has declined to 5 francs, and even less, the zinc works having more demand from acid makers than they have blende to be desulphurised. This desire on the part of the acid makers to roast blende, due to the sensible difference in the cost price of the acid, has been developed since the introduction of the Delplace furnace, which may be employed at choice either for blende or pyrites, the fires being extinguished in the latter case.

[I have thought it right to reproduce the paper of M. de Lummen (about whose personality nothing is stated in the *Chem. Trade J.*), in detail, in view of its interest, but it is hardly necessary to say that I entirely repudiate any responsibility for his statements, whether they are laudatory or the reverse, as well as for the manner in which they are framed.—G. L.]

Page 512. *Testing the Cinders from Roasting Blende.*—This subject is briefly treated on pp. 511 *et seq.*; we here give some details on it.

colour produced on the paper they judge of the state of roasting.

Max Liebig (*Zink und Cadmium*, p. 34) dissolves 2 g. of the cinders in aqua regia, by slowly heating in a flask, placed on a sand-bath in a slanting position. He then evaporates to dryness, dissolves in water acidulated with hydrochloric acid, filters, dilutes to 200 c.c., places all the samples on a dark plane, adds an excess of $\frac{5}{10}$ normal barium chloride solution (of which, when working on 2 g. cinders, each cubic centimetre indicates ½ per cent. S) and notes the number of seconds elapsing until the appearance of an opacity which admits of judging on the sulphur contents.

The same author estimates in samples containing 2 per cent. S or upwards the sulphur by the method of Wildenstein (Lunge-Keane's *Technical Methods of Chemical Analysis*, vol. i. p. 278), consisting in running in a solution of barium chloride, with application of a bell-jar filter. The solution contains per litre 76·25 g. $BaCl_2,2H_2O$, and 1 c.c. of it when working on 2 g. substance indicates 0·5 per cent. sulphur.

(b) *Accurate methods.*—The estimation of the sulphur is carried out volumetrically by the method of Lunge and Stierlin (p. 298). In the presence of very much zinc it may happen that, in consequence of the secretion of zinc oxide and carbonate during the titration, an opacity is produced which makes it difficult to recognise the exact point at which the colour of the methyl-orange is changed to the "intermediate" point. In such cases it is preferable to carry on the titration, both of the pure bicarbonate and that of the solution finally obtained, until the indicator shows a decided *red* colour.

In the case of cinders containing upwards of 6 per cent. sulphur, the mixture is made as follows:—1·603 g. cinders, 2·000 g. sodium bicarbonate, 4 g. potassium chlorate, 2 or 3 g. ferric oxide, free from sulphur. If we designate the conbe understood. The difference $a-b=c$ shows the sulphur still present in the cinders in the shape of zinc sulphate (d) and and zinc sulphide (e). Since it is uncertain whether those metals are really present in the cinders in the shape of sulphides, Hassreidter (*Z. angew. Chem.*, 1906, p. 137) recommends the direct estimation of the "injurious" sulphur, c, by estimating the sulphur of zinc sulphate, d, and zinc sulphide, e; therefore the sum $d+e$, in the following manner:—

Sulphur of Zinc Sulphate (d).—Extract in a ¼-litre flask 25 g. of the cinders with water, fill up with water after cooling, filter, and estimate in 200 c.c. the zinc (+ any cadmium present) by the method of Schaffner. 65·37 parts of zinc correspond to 32·07 parts of sulphur present as zinc sulphate.

Sulphur of Zinc Sulphide (e).—Extract 2 or 3 g. cinders with a solution of 30 g. pure zinc in 1 litre of hydrochloric acid of sp. gr. 1·19, in a flask with reflux cooler at boiling-heat, and pass the H_2S thereby quantitatively liberated into a test-bulb, charged with 30 to 40 c.c. of a solution of bromine in hydrochloric acid, which causes the conversion of the H_2S into sulphuric acid. Brominated hydrochloric acid is for this purpose preferable to hydrogen peroxide, because it admits of following the progress of the reaction in the test-bulb by the gradual decolorisation of the reagent, so that it is always possible to recognise whether the oxidising agent had been employed in the necessary excess. After removing the excess of bromine and approximately neutralising the hydrochloric acid with sodium carbonate, the sulphuric acid is precipitated by barium chloride.

Some descriptions of blende contain aluminates and silicates of zinc which pertinaciously resist the action of aqua regia.

Lindt (*Metall und Erz*, 1915, p. 335; *Z. angew. Chem.*, 1915, ii. p. 613) describes the injurious effect of the sulphur of

Z. angew. Chem., 1912, p. 860.

Hybinette (Ger. P. 275204) adds to cupric-sulphide ores from 2 to 5 per cent. sodium sulphide before roasting; this prevents the formation of hard lumps of cupric sulphide, which are not dissolved in the succeeding treatment with ferric salts.

The U.S. P. of Carmichael (whose German patent is mentioned on p. 514) is No. 1124696.

Offerhaus (*Metall und Erz*, x. p. 863; *Z. angew. Chem.*, 1914, ii. p. 442) describes the "pyritic process" for smelting copper ores in kilns, in which ferrous sulphide, FeS, serves as fuel; in the "semipyritic process" coke is used at the same time. At Copperhill factory part of the furnaces is connected with a sulphuric acid plant, consisting of twenty-four large and eighty small chambers, and eleven Gay-Lussac towers, with a daily production of 600 tons sulphuric acid of 60° Bé.

According to Dempwolff (*Metall und Erz*, 1914, p. 619; *Chem. Zeit. Rep.*, 1915, p. 127), on heating lead sulphide up to 450° principally lead sulphate is formed; at higher temperatures more SO_2 is formed, but no SO_3. When all the lead has been converted into sulphate, all stages in the proportion of SO_2 : SO_3 are gone through, until at 760° the proportion 65 SO_2 : 35 SO_3 has been attained. If the temperature is raised still higher, besides the oxidation also reduction sets in. By the admixture of indifferent substances the limit of the reaction can be moved on even to higher temperatures.

G. de Bechi (B. Ps. 9939, 1906, and 4246, 1912) separates in mixed sulphide ores the lead and zinc by converting the sulphides into sulphates. The finely ground ore is treated with a hot solution of ferric sulphate, containing free sulphuric and nitric acid, whereby PbS and ZnS are converted into sulphates, the ferric sulphate being reduced to ferrous sulphate, *e.g.*, acid required for the process is regenerated; the residual ZnO is converted into metallic zinc. The free sulphur is obtained by distillation or extraction by means of a suitable solvent, and the final residue, which contains all the lead, is converted by the ordinary smelting process into silver-containing metallic lead.

Reinders (*Z. anorg. Chem.*, 1915, xciii. p. 213; abst. *J. Soc. Chem. Ind.*, 1916, p. 847) describes the reactions taking place in the roasting of lead sulphide.

Estelle (Ger. P. 293908) treats the sulphide ores with hydrochloric acid; the iron is dissolved in the ferrous state and the sulphur escapes as H_2S. The ferrous chloride is lixiviated out and electrolysed, whereby part of the iron is separated in the metallic state, and the remainder is brought into contact with the H_2S, whereby the sulphur is precipitated, and the ferric salt is reduced to the ferrous state.

Debusch (Ger. P. 269774) treats pyrites containing copper, zinc, and lead sulphides as follows. The roasting process is interrupted, for part of the material, and the product mixed with the other part to be finished at a later stage. In order to moderate the excessive heat caused by the roasting, other materials may be mixed with the pyrites which do not participate in the roasting. Thus it is attained that the metals accompanying the iron are converted into an easily soluble state, *e.g.* into sulphates. The roasting is effected at 600° to 650° by moving part of the ore from the first shelf to the third, from the second to the fourth, and so forth.

According to B. P. 14295, 1914, of Wade (a communication from Carmichael and Montgomery), sulphide ores of low sulphur content are roasted so as to sulphatise one or more of the metals present, and at the same time to produce a furnace-gas rich in sulphur dioxide. The ore is heated to the required of Huntington and Heberlein (p. 514), of Dwight and Lloyd p. 515), of Godfrey and of Wedge (p. 495). The last two systems work with ores containing a good deal of sulphur (25 to 35 per cent.), the Dwight-Lloyd furnaces with poor ores (15 to 18 per cent.) which cannot be used for the furnaces of Godfrey and Wedge. For the Dwight-Lloyd and the Huntington-Heberlein furnaces the ores must go through a preliminary roasting, or the sulphur contents of the ore must be got down by admixtures; these two furnaces are therefore finishing roasters, the other two preliminary roasters. The Dwight-Lloyd plant roasts per diem 220 tons ore of 15 to 16 per cent. S down to 4 per cent.; the Huntington-Heberlein plant, 400 tons of 17 to 19 per cent. S down to 5 per cent. The cost of roasting of the last-mentioned works are lower by 3 to 4 cents, but the cost of plant is higher. At the former there was 0·93 per cent. lead in the scoria, and 14·96 per cent. in the matte; at the second, 0·63 per cent. lead in the scoria, and 10·7 per cent. in the matte. As to the physical properties, the Huntington-Heberlein product is superior.

D. SULPHUR DIOXIDE FROM VARIOUS OTHER MATERIALS.

Utilisation of the Sulphur contained in Coal-gas.

Page 517. Mackenzie (B. P. 4770, 1913) passes the gas, after taking out the ammonia, through ferric oxide. When this is saturated with sulphur compounds, hot air is passed through, while also applying heat from without, and the resulting mixture of SO_2 and SO_3 is completely transformed into sulphuric acid by means of a spray of sulphuric and nitric acid in a tower like the Glover tower. The gases issuing out of this are passed into a lead chamber and a Gay-Lussac

Dealing with the Sulphur Dioxide from Acid-smoke, Fire-gases, etc.

Page 520. H. Wislicenus (*Die Abgasfrage*, 1912) asserts that sensitive plants, like pine-trees, are damaged if there is as little as 1 part SO_2 (or total acids calculated as SO_2) in 500,000 parts of air, and if they are exposed to such air during a whole period of vegetation. That limit is far exceeded by the air of industrial regions in spite of all remedies hitherto tried, and even the giant chimneys built in some places have not had any success, whilst he claims this for his "dissipators" (see below). The injury done by acid gases principally extends to the chemical processes of assimilation; chlorophyll is destroyed even by minimal quantities of SO_2, and the protoplasma is also acted upon.

In the special catalogue of the group, "Injury by smoke," of the International Hygienic Exhibition at Dresden in 1911, Wislicenus enumerates the literature on this subject, which has an enormous extension, and whereof his own publications form an important share. In that place he also discusses the causes of the damage done by the smoke, and the measures or proposals for its prevention. In his pamphlet on the foundations for technical and legal measures for the prevention of damage by smoke (Berlin, 1908), he had already come to the conclusion that the removal of SO_2, strongly diluted with combustion gases by washing with water alone, has no prospect of success, much more the combination of that washing with sprinkling with lime in towers or chambers. He enters fully into this matter, but he considers it as too expensive. He especially treats of the prevention of damage through smoke gases by diluting them with air or other indifferent gases. To this refers already the proposal made by him in Ger. P. 134000 taken out with Isaachsen and mentioned in our text principle for dealing with the smoke gases is their dilution with air. But, wherever this has been tried on the large scale, it has been found that blowing air into the chimneys is not suitable, since even the best apparatus for this purpose work too expensively. Apparatus for blowing or aspirating air work even then uneconomically, if they have only to provide the air indispensable for combustion. The modern installations for "artificial draught" introduce air only to the extent of one-half, or at most three-quarters of the volume of the smoke gases, and therefore dilute these only by 50 up to 75 per cent., which is not sufficient. When the gases get into the free air, undoubtedly at first a further manifold dilution takes place, as long as the gases are still in a whirling condition, *i.e.*, as long as their temperature and movement are different from the air. But if the air-current moves on evenly, the air and the smoke gases will soon come to equal velocity, temperature, and direction. Where there is no interruption by differences of level, houses, trees, etc., the smoke gases will travel on without being sufficiently diluted, and after a long way through the air, will still descend as poisonous fumes upon the soil and the vegetation.

This uniform motion, without whirling, must be especially avoided. We know from experience, *e.g.* from the observations of aeronauts, that all valleys cause strong whirls in the air-currents above them. Higher up the air-current generally proceeds evenly. It is, therefore, a mistake to introduce the smoke gases into these high, not whirling air-currents. Chimneys, which from hygienic regards are built much higher than required by their function of producing draught, are therefore inoperative; they protect at most their immediate surroundings. The task is therefore: taking care to produce at the source of the smoke itself a sufficient dilution and formation of a whirling movement. That is also the principle of the variety of directions and speeds. At first some practical men called it nonsense to build a chimney with holes. To this Wislicenus remarks that, as a matter of course, there must be a sufficiently high draught-producing shaft, if the chimney itself has to provide the work of draught. But there are some cases where there is no aspirating work required from the chimney, but where this is performed by artificial means, such as fan-blasts, exhausters, etc. Only the "hygienic" part of the chimney, which has frequently caused it to be made much higher, is to be replaced by a lower, but more efficient, dissipator, which causes the formation of *whirls* and the admixture of air during the *outflow* of the gases. Through the variously directed channels in the wall the diluting air is introduced at the wind side with various velocities and in various directions. On the other, the "lee" side, the wind will act in an aspirating way. In such cases where there are not tall chimneys, but gas outlets, from dehydrating plants, flue-dust chambers, etc., the outgoing gases are still more diluted with air by a "multi-dissipator." The gases are gradually divided and diluted. Since from the lowest series of wind-channels only a small fraction of the gases escapes, with which from the opposite side more wind is mixed, the main body of the gas must rise higher upwards, and gradually mix with more air. Consequently there is both a mechanical and a temporary dissolving action. Into iron chimneys the wind-channels may be introduced tangentially.

At first the chimneys were built in such manner that the holes were produced by leaving interstices between the bricks. This has certain drawbacks, especially an excessive contact of the joints with acid gases. Therefore later on perforated stones have been employed, in which the air-channel goes through the body of the stone, and the joints are as little as possible in contact with the smoke gases. But the mortar-joints may also

The inventor has recently, in connection with the Metallbank und Metallurgische Gesellschaft at Frankfurt a.M., applied a very fine sieve-grating, made of perforated stones.

After the lecture given by Wislicenus in 1911, a practical chimney-builder made the objection that the numerous holes in the upper part of the chimney-shaft are strongly exposed to frost, rain, etc., so that the material must greatly suffer, and frequent repairs will be required, about which point further experience must be collected.

According to Reuss (*Rauch und Staub*, 1914, p. 162), it is true that in the case of faintly acid gases and small quantities of smoke the gases going out from high chimneys may be diluted up to being quite innocuous, but, under certain circumstances, high chimneys may have an injurious action, by carrying the gases to much greater distances and affecting a much greater extent of forest.

Reports on the damage done by coal-smoke in the Rhenish-Westphalian industrial district have been made by Eicke (*Rauch und Staub*, 1913, p. 162) and Rippert (*Glückauf*, 1912, pp. 1992 and 2026).

Moscicki (Ger. P. 256595) employs for absorbing the acids from large quantities of diluent gases by liquids a space in which the liquid flows through a packing, contained in a single space, through which the gases travel in the horizontal direction. The packing is divided into layers, perpendicular to the direction of the gas-current, some of which are sprayed with water. This division is produced by a number of partitions pervious to the gases, which prevent the descending liquid getting from one layer to the next, so that the liquid gets more concentrated in the places near the entrance of the gases.

Flasche (Ger. P. 271786) describes an absorbing-vessel with tangentially arranged tubes for introducing the gas.

Zschokke (Ger. P. 283088) describes an apparatus for purifyblasts for producing the draught, the loss of SO_2 may go up to 15 or 20 per cent. This is, according to de Cew's U.S. P. 1077243, avoided by filling the top part of the limestone tower with moistened blocks of calcined magnesia. The magnesia is not, like the lime, converted into hydrate, and absorbs SO_2 even in the most highly diluted form much more easily than lime, with formation of magnesium sulphite and bisulphite.

Bauxite, or similar substances, are employed by Peniakoff (B. P. 21476 of 1912; Fr. P. 459926). The acid gases, preferably still hot, are brought into contact with the purifying materials, which are best moved forward in a direction opposite to that of the gases. The sulphur acids contained in these are thereby fixed in the shape of sulphate of alumina and iron, which are obtained by lixiviation, and are either worked up into a marketable state, or decomposed by heating into sulphuric acid and a residue again serving as absorbent.

Page 529. *Absorption of* SO_2 *by Charcoal.*—Exactly the same process as that of Allen, described in our text, is described in the U.S. P. 1145579, of Garner (Metals Research Co.).

Garner and Clayton (U.S. P. 1173566, assigned to the Metals Research Co.) treat SO_2 with a gaseous fuel containing carbon monoxide and hydrogen, in presence of wood charcoal at a temperature of 500° to 600°, whereby H_2S is formed.

Murray and Ricketh (U.S. P. 1132679) pass air containing sulphuric acid fumes through a thin sheet of sodium carbonate solution, then with the entrained liquid through an adjacent foraminous screen, and finally through a second parallel sheet of sodium carbonate solution.

Page 530. The SO_2 contained in the waste liquids from the manufacture of paper pulp made by the bisulphite process described by Martin in *Met. Chem. Engin.*, xii. p. 709 (1914). The ores used there are pyrites containing 3 to 5 per cent. copper, 4 to 5 per cent. zinc, and a little gold and silver; they are worked in blast-furnaces. The outgoing gases first pass through dust-chambers, where they are cooled and mixed through, and part of the dust is deposited. When going out, their temperature is still at 280°. They now pass through a set of fifty cooling pipes, whereby their temperature goes down to 130°; by dilution with cold air they are cooled down to 99°, and now pass into the "bag-house." This is 220 ft. long and consists of twenty compartments, each of them containing 148 bags, forming a total of 2960 bags. These are made of pure wool, and are 34 ft. long and 18 in. wide. The acids contained in the gases are partially neutralised by the zinc oxide formed in the blast-furnaces, partly by hydrated lime during the cooling. On leaving the bag-house, the gases must contain no trace of dust or SO_3, and their contents of SO_2 has gone down to 0·4 to 0·5 per cent. The dust accumulating in the bags contains lead, zinc, silver, gold, and other metals; up to the present no suitable method for working it up has been found. Only a small portion of it is converted into briquettes and charged again in the furnaces; most of it is thrown on a heap near the works, where at that time already 16,000 tons of it had accumulated.

Schiffner (*Metall und Erz*, 1914, p. 257; *Z. angew. Chem.*, 1914, ii. p. 978) describes several processes for dealing with the acid-smoke, on which experiments had been made at the Freiberg Mining Academy, especially Young's thiogen process (p. 13), and the processes of Hall (pp. 9 and 16) and of Cottrell (p. 9).

According to a report of the U.S. Geological Survey (mentioned in *Chem. Trade J.*, 1914, p. 284) in the United States the sulphuric acid produced by copper and zinc residue, either by a flame containing an excess of air, or by the successive action of a reducing flame and oxygen (preferably in the shape of air). The process may be applied to sulphides, the heated material being decomposed by an oxidising flame or by air.

Preparing Solutions of Sulphurous Acid or of Sulphites.

Page 531. An apparatus for preparing *solutions of sulphurous acid or of sulphites* is described by F. E. Coombs (U.S. P. 1147376). It comprises, first, a brimstone furnace with a shallow bottom tray, fired from below, and over this a funnel for the brimstone to be burned, provided with a steam mantle by which the brimstone can be fused and run down into the furnace, regulated by a tap. The SO_2 gases pass into the lower part of an absorbing-cylinder, filled with suitable dividing materials, over which water, milk of lime, a solution of sodium carbonate, etc., is run. At the bottom it is funnel-shaped, and the solutions obtained run into a receiver. This contains a float by which the pumps for feeding the absorber with liquid and for carrying away the solution formed therein are automatically regulated.

Sulphur Dioxide in the Pure and Liquid State.

Page 533. Humphries (B. P. 10810, 1912) obtains pure SO_2 by drying both the sulphur-containing raw materials and the air previously to the roasting, and filtering the SO_2 through concentrated sulphuric acid.

Nonnet (B. P. 26999, 1912; Fr. P. 450804) adds to a mixture of equal parts of alkaline bisulphite and sodium thiosulphate, fused in its water of crystallisation, 5 per cent. of gum arabic, and then the equivalent quantity of anhydrous sodium thio-

Moore and Wolf (U.S. P. 1091089) pass SO_2 gas, produced in any suitable way, containing air and nitrogen, into a cooled solution of calcium chloride, which retains the SO_2, and from which it can be obtained in the pure state by heating with application of a vacuum. The advantage of employing a solution of calcium chloride instead of pure water is this: that it can be cooled down below 0° without solidifying, and that its boiling-point is higher than that of water. Since the boiling-point of the dissolved SO_2 in both cases is the same, less water is carried away with it when driving it out of the solution of calcium chloride than when driving it out of a solution in water.

Mather (Ger. P. 261506) describes a vessel for keeping liquids or gases under pressure.

In Germany the production of liquid sulphur dioxide in 1909 was 5804 tons; in 1910, 6951 tons; in 1911, 7456 tons.

In Eastern Borneo there is a factory for producing 4 tons of sulphur dioxide per month, for use in the manufacture of ice (*Chem. Zeit.*, 1916, p. 80).

Olga Niedenführ (Ger. Ps. 254044 and 254362) aspires part of the already liquefied sulphur dioxide, and employs the gaseous SO_2 thereby formed for producing sulphur dioxide in the concentrated state.

Page 539. *Carriage of Liquid Sulphur Dioxide.*—Meves (Ger. P. 292727) employs a vacuum vessel for this purpose.

Page 540. *Use of Liquid Sulphur Dioxide.*—According to Edelenau (*Bull. Amer. Min. Eng.*, 1914, p. 2313), liquid sulphur dioxide is employed in the refining of petroleum. It dissolves the non-saturated hydrocarbons which cause the bad burning or the characteristic smell of some lighting-oils, and leaves the an apparatus for mixing liquid sulphur dioxide with air for disinfecting purposes.

Fischer and Glund (*Berl. Ber.*, 1916, p. 1469) employ liquid SO_2 for extracting organic substance from coal.

Treatment of the Burner-gases.

Page 543. The Badische Anilin- und Sodafabrik (Ger. P. 287471) cool the gases first rapidly by indirect cooling to 40° to 65°, separate the resulting weakly acid water, and catch the spray of sulphuric acid on dephlegmating plates, whereby acid of 40° Bé. is obtained.

Page 543. Herreshoff (U.S. P. 1113437, transferred to the General Chemical Company, New York) dries the burner-gases by treating them with dilute sulphuric acid, rapidly cooling them from 93° down to 38°, and removing the condensed liquid.

Cellarius (Ger. P. 263941) obtains steam for working purposes by utilising the heat of the gases of pyrites and blende burners. In the gas-flue a closed vessel is placed into which, from outside, water is squirted by means of a spray-producer, the steam thereby formed being carried away by a pipe from the top of that vessel. Two or more such vessels may be placed in the flue, the steam-pipes of which are connected with a common collector. Behind these vessels another vessel may be placed, into which no water is sprayed, for the purpose of superheating the vapour passing through it. The vessels may consist of cast iron, with a suitable lining and a layer of fireclay lumps at the bottom. By this means the steam for producing the power required for driving the mechanical burners, fan-blasts, air-compressors, etc., may be partially or entirely obtained.

Removal of Flue-dust.

with filters made of perforated tubes, open at both sides, and lateral gas inlets and outlets. The perforated tubes are suspended from the roof of the chamber, and are accessible to the gases on all sides. If their perforations are too much stopped up, so that the draught is interfered with, the gases can take their way from below through the tubes, at whose walls some dust always adheres.

The Gräflich von Landsberg-Velen und Gemensche Chemische Fabrik (Ger. P. 256237) pass the burner-gases first through a dry filter, then through a denitrating Glover tower and through a series of wash-towers, fed with acid as free as possible from arsenic. That acid, after having taken up a sufficient quantity of impurities, is employed for feeding the Glover tower. The dry filter has a slanting bottom on which the granular filtering material slides forward; the gases pass into it from below and from the side.

The Gewerkschaft Messel, Adolf Spiegel und Paul Meltzer (Ger. P. 260415), pass the gases through wires, extended between the two perforated ends of a cylinder, revolving in a fixed case. At the gas outlet of the non-perforated part of the cylinder bottom a revolving fan produces between the casing and the revolving cylinder a plus-pressure, which leaves to the gas only the way through the wires.

Boubon (B. P. 15209 of 1911) passes the gases under pressure into a revolving cylinder, containing plates at whose circumference they escape through holes. The dust is here washed out by water or some other liquid.

Liebrecht (Ger. P. 265584) passes the gases through pieces formed from crystalline materials, together with steam.

Fr. Curtius & Co. (Ger. P. appl. C23027) wash and filter the gases in towers, regulating their temperature in such a way that they take up a quantity of water or acid, sufficient for an acid-proof material, prepared by gradually heating cotton tissue, weighing 350 g. per superficial metre, in closed vessels to 300° to 350° for some minutes, or to 200° to 250° for several days, and subsequently cooling. The tissue loses 68 to 76 per cent. of its weight, and its tensile strength falls from 2300 kg. to 30 to 35 kg. per metre, but this still leaves sufficient flexibility to the fibre. The carbonised product contains considerable proportions of chemically combined hydrogen and oxygen, and is a good conductor for electricity.

Else Heine (Ger. P. 280088) passes the gases through the mixing tuyere of a steam- or water-spray producer, whereby the solid particles are moistened and partly compressed, partly torn up; on the water-spray striking against a wall, they adhere to this, or are taken away by the water running out. Behind this wall a contrivance for separating liquids may be placed.

Reichling (Ger. P. 279819) describes an apparatus for separating solid and liquid particles from gases and vapours, containing adjustable longitudinal partitions.

Moore (U.S. P. 1184006) filters the gases through a series of fabrics which are periodically cleared of dust; the last filtering-fabric is allowed to remain filled with dust, whereby the last traces of dust are removed from the gases.

Brunner & Co. (Ger. P. 269539) remove liquids from gases and vapours by passing them through a series of rods.

Page 553. Further proposals for effecting the removal of flue-dust are described in the following patents:—Gerdts and Strauch (Ger. P. 257368); C. S. Watson (B. P. 17384, 1912); Neumark (Ger. P. 263285); Greding (Ger. P. 263201); Püning (Ger. P. 262882); A. Müller (Ger. Ps. 216483, 265638); Kirschner (Ger. P. 268880); Krowatschek (Ger. P. appl.

kind of burners, and upon the fineness of grain of the blende. An average sample of the flue-dust showed: 6·54 per cent ZnO; 24·29 $ZnSO_4$; 6·75 Fe_2O_3; 6·80 $FeSO_4$; 5·37 $Fe_2(SO_4)_3$; 11·61 $PbSO_4$; 12·84 $CaSO_4$; 7·18 $MgSO_4$; 0·25 As_2O_3; 8·16 SiO_2; 0·40 Tl_2O. The proportion of sulphates to the oxides, especially of iron and zinc, seems to be greatly dependent upon the temperature reigning in the dust-chamber, and the composition of the gases. The flue-dust not retained in the dust-chambers gets into the Glover towers; here the oxides are completely converted into sulphates, and these are partly deposited on the packing of the tower in constantly increasing crusts, but mostly carried away by the Glover acid, and only deposited in the acid reservoirs, coolers, and spreading apparatus, whence they must be removed from time to time. With the Glover acid the sulphates get into the Gay-Lussac tower, and here also gradually obstruct the packing. Crusts of sulphate are also deposited in the lead tubes for pumping the acid. A small portion of the flue-dust gets into the vitriol chambers, where it is precipitated together with the acid fog, and saturates the chamber-acid with sulphates; the insoluble lead sulphate accumulates in the chambers as mud. A muddy sulphate formed in an iron acid reservoir had the composition

$$Fe_2(SO_4)_3 \cdot 3H_2SO_4 \cdot 8H_2O,$$

in crystalline crusts the compound

$$Fe_2(SO_4)_5 \cdot H_2SO_4 \cdot 7H_2O$$

was contained. The same was found in larger, well-formed, greenish yellow crystals on the inner walls of lead pipes leading out of the coke-boxes of a Gaillard concentrator. The lead sulphate is less inclined to form acid sulphate; that contained in the chamber mud is normal sulphate. In concentrated acids recuperator of a Gaillard concentrating apparatus (p. 1203) once a salt mass was found, composed of

$$Al_2(SO_4)_3, H_2SO_4, 14H_2O.$$

The $ZnSO_4$ remains mostly dissolved in the hot Glover tower acid, but crystallises on its cooling in the Gay-Lussac towers. In the concentrating apparatus the author also found a hitherto unknown acid zinc sulphate of the formula

$$ZnSO_4 . 3H_2SO_4.$$

Page 556. *Removal of Selenium from Burner-gases.*—Klason and Mellquist (whose paper is quoted in the text, p. 545) remove the selenium by a tight filter, made of asbestos or the like, and recover it from this by heating or by means of a solvent.

Composition of the Gases produced in Burning Pyrites.

Pages 567 and 569. According to L. T. Wright (*J. Soc. Chem. Ind.*, 1914, p. 111), the deficiency of oxygen noticed by Scheurer-Kestner, Bode, and Lunge, in their analyses of pyrites-burner gases, is all the greater the more strongly the gas is diluted; this, he considers, points to the fact that, apart from the well-known absorption of oxygen by the formation of sulphur trioxide and of metallic sulphates, there must be another cause for that deficiency, perhaps a constant error in the methods of analysis. Anyhow, even when the oxygen is completely consumed, the percentage of SO_2 in the burner-gases cannot exceed a maximum of 12 per cent., as his own practical trials have proved.

Page 564. *Estimation of* SO_2 *and* SO_3 *in Roasting-gases,* paper being put in between; here the SO_3 is retained, which is then washed out of the paper and titrated with decinormal soda solution and methyl-orange.

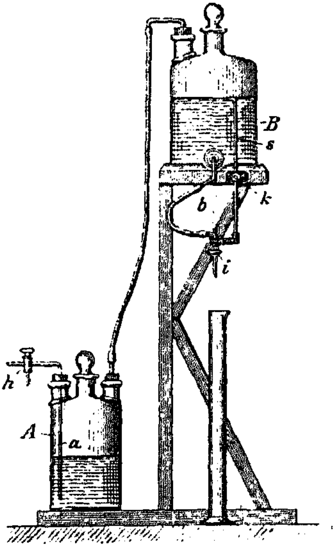


FIG. 9.

Page 573. *Estimation of the Sulphur Dioxide in Burner-gases.*—Ljungh (*Chem. Zeit.*, 1909, xxxiii. p. 14) describes a useful modification of the Reich apparatus, by means of which any requisite corrections of pressure can be effected in a simple manner. This apparatus is shown in Fig. 9. The running-off tube *b* of bottle B is turned in an angle, and is connected by an india-rubber tube with the tap *i* fixed at the bottom end of the perpendicular metal rod *s*. The top end of *s* is turned in a right angle, the point of which serves for adjusting the rod to the changing level of water in B, by means of the clamp-screw *k*. A test for SO_2 is made as follows:—By opening tap *h* on bottle A, the tube is filled with fresh gas, and at the same time a measured quantity of iodine solution is put into A. After closing A, tap *i* is opened and the point of rod *s* is adjusted to the level of water in B. Now, by turning tap *h*, the gas is passed through *a* into the iodine solution contained in A. The non-absorbed portion of the gas passes into the bottle B; the water displaced by it is caught in the cylinder below *i*. At the moment when the iodine solution in A is decolorised, The absorption flask, described in the *Thirty-fourth Report of the Inspector of Alkali Works*, 1897, p. 22, is shown in Fig. 10. It cannot be used for the Reich test, as the india-rubber would act upon the iodine solution, but it gives good results in the Lunge test for total acids, and in other very difficult cases, such as the absorption of acid fog. The figure shows it in one-third of the actual size. The flask is fitted with a rubber stopper provided with an inlet- and exit-tube. The former is 8 mm. wide, closed at the bottom, and pierced with a number of small holes, through which the gas passes to a double bulb, attached to the tube by means of a rubber stopper. The upper bulb is filled with small cuttings of rubber tubing, kept in motion by the stream of gas, which is thus brought into very intimate contact with the absorbing solution; the lower bulb is open at the bottom. The success of the operation depends largely on the correct dimensions being adhered to. The lower opening of the double bulb is 6 mm. in diameter, the lower bulb is 15 mm., and the upper bulb 18 mm. in diameter; the upper opening, through which the inlet-tube passes, is 13 mm. wide. The gas passes from the bulb into the flask through several small holes, and finally leaves it through the exit-tube, which is narrowed below, and widened above, to form a cylindrical chamber; the lower, narrow portion is filled with

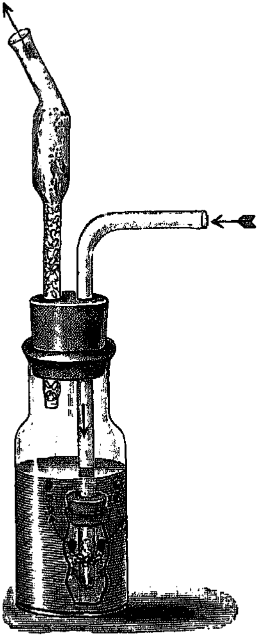


FIG. 10.

When used for the absorption of acid vapours, the exit-tube is moistened with water coloured by methyl-orange, which serves to indicate whether complete absorption is being effected in the bottle.

Lunge (*Z. angew. Chem.*, 1890, p. 567) has also proposed to determine the acidity of burner-gases by measuring their specific gravity, a method which might be used for giving a continuous graphic record of the operation of the burners. Differences of 1 per cent. of SO_2 by volume affect the value of the specific gravity in the second decimal place; differences of 0·1 per cent. do this in the third decimal place. Such measurements might be made, *e.g.*, by a modification of the Lux gas balance, which, as at present constructed, is not suitable for use with acid gases.

Nestell and Anderson (*J. Ind. Eng. Chem.*, 1916, p. 258) absorb the acids in flue gases by sodium carbonate solution, and retitrate this, using methyl-orange as indicator. The residual Na_2SO_3 is oxidised by hydrogen peroxide.

Page 578. *Estimation of Oxygen in Burner- and Chamber-gases.*—The absorption of oxygen by *pyrogallol* can be carried out by a Winkler gas-burette, or by an Orsat apparatus, etc. Very convenient for this purpose is the apparatus constructed by M. Liebig (*Dingl. polyt. J.*, ccvii. p. 37), which allows of making an estimation in three minutes. This apparatus (which is made by Dr Geissler, at Bonn) may also be used with other absorbing agents for other gases, *e.g.* with caustic-potash solution for carbon dioxide. It works more quickly than Winkler's gas-burette, but does not, like this, allow of making a full analysis of gases with the same sample. For this purpose Liebig has constructed another apparatus, about which we must refer to his paper (*loc. cit.*, p. 44).

It has been proposed to purify the gas from any sulphur

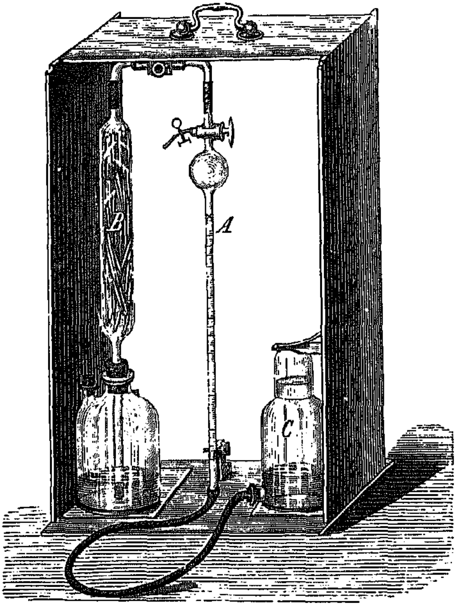


FIG. 11.

into tenths of a cubic centimetre. The level-bottle C contains water, the absorbing-vessel B, thin sticks of phosphorus and water up to the mark. The gas is introduced through the pinchcock arrangement connected with the three-way cock. The manipulation is exactly as with Orsat's apparatus.

CHAPTER V

CONSTRUCTION OF THE LEAD CHAMBERS, TOWER SYSTEMS, ETC.

Page 597. *Burning the Lead Joints.*—In the text the usual statement is made that the construction of lead joints by burning had been invented in 1838 by Debassayns de Richemond. But E. von Lippmann (*Chem. Zeit.*, 1912, p. 437) has shown that this process was already known in the Middle Ages, and perhaps even in ancient times.

Page 605. *Lead Straps for carrying the Chamber Sides and Top*—Kalinowsky (Ger. P. 260991) describes carrying-lashes, firmly grasped by the lashes burnt to the chamber walls, which are fastened by means of hook screws on iron rods or tubes in such a way that they can be moved and turned. The carrying iron rods or tubes are placed in beams provided with slots, in which they can be moved backwards and forwards.

F. A. Neumann (Ger. Ps. appl. M 14024 and 14025) suspends the chamber sides by means of horizontal lead straps from horizontal iron rods fastened to perpendicular rods which are carried by the stays arranged outside and between the chambers, with intermediate parts, but quite independently from the roof frame (which is an essential point). The perpendicular rods may be connected by transverse rods. This construction makes the chamber top more accessible vitriol chambers on horizontal rods, avoiding a special chamber frame by suspending the lead sheets by means of rods independently of the roof of the building, which can be altogether done away with. His specification runs as follows.

The hitherto known forms of iron chamber construction, allowing of suspending the lead sides and top of vitriol chambers without a regular frame, were all depending on the presence of a roof, as this was required for bearing all the arrangements for suspension. But circumstances may arise which make it necessary or advisable to choose the form of the roof and its strength independently of the iron construction carrying the sheets of lead, or even to dispense altogether with a roof, as is usual in countries with a suitable climate, without abandoning the advantage of a free suspension of the lead sheets—that is, without a chamber frame in the ordinary sense. This is made possible by the construction shown in Fig. 12 (*a* to *d*). The lead sheets are supported by the trestles, *a a*, in the shape of lattices, or in other ways, preferably made of iron; but other materials, *e.g.* wood, may also be used. The trestles, *a a*, are kept in the proper position by stays, *b b*, at their upper side. The roof of the building, *c*, rests on the trestles, but it may be dispensed with altogether. The lead sheets of the chamber, *h h*, are provided with straps, *d*, through which pass the horizontal rods *e*.

The Metallbank und Metallurgische Gesellschaft A. G., of Frankfurt a.M., which has carried out that invention on a very large scale, points out that it makes it possible to build *high* chambers with all their advantages, and it also admits of repairing the lead sheets in any place, as they are accessible everywhere. If any of the iron-suspending parts suffer damage, they may be replaced by new ones without any interruption of the work. The chamber frame itself is kept away from the curtain, and its other end, shaped like a U, fits into a

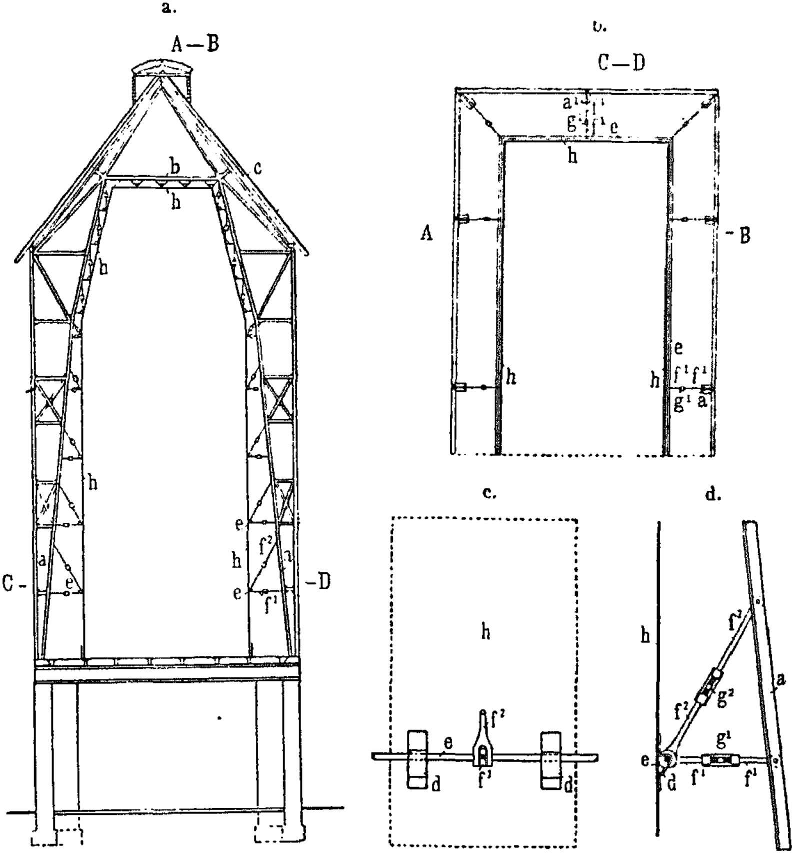


FIG. 12.

radially between a central ring and the outer framework. A pipe or flue may pass from or into the chamber.

Nemes (B. P. 24223, 1913) strengthens both the sides and the bottom of the chambers by iron supports, arranged in such a way that any leakages occurring in the chamber bottom, especially in the corners, are immediately discovered before they have corroded the iron. The lead straps for holding the chamber sides surround the upright column of the iron framework, and rest upon projections provided on those columns. The lead chamber bottom is not strengthened from without by sheet iron, but rests on an iron framework attached to the columns, whereby the chamber bottom is cooled and made accessible in all places. It rests upon a wooden floor, which allows of easily noticing any leakages of acid.

Seeck (B. P. 16187, 1914; Fr. P. 474502) suspends the lead sheets from flat iron rails, tubes, etc., resting freely on hooks suspended on bearers. The hooks may be placed at any desired height; they are in a right angle to the sheets of lead, and touch these only in one point.

Petersen (Ger. P. 295044) describes special arrangements for supporting the lead sheets.

Special Forms of Vitriol Chambers.

Page 627. Kalinowsky (Ger. P. 265640) constructs vitriol chambers with several contractions of the horizontal axis which at both sides lead gradually up to the full horizontal section, with avoidance of dead corners; these narrowed places contain perforated diaphragms over which reacting liquids are run down.

Ising (Ger. P. 267513) aims at preventing the rapid destruction of the chamber walls by acid condensing upon them, which gets mixed with lead slime and runs down; this causes a rapid corrosion of the lead, all the more the more acid runs the following ones, 4, 3, 2 cm., and the bottom one, 1 cm. This arrangement will render good service especially in the "intensive style" of working the chambers (*v.* our text, p. 639).

Littmann (Ger. P. 271077; Fr. P. 462668; Austr. P. 60969) builds vitriol chambers of the form sketched in Fig. 14. The main chamber H and the intermediate chamber M are made successively lower, in order to counteract by the diminution of the section any lowering of the activity of the gases through too great a separation; also in order to promote the reaction by shocks of the gases (surface condensation) not merely against the back wall, but all along the length of the chambers. In the main chamber H the surface and the cooling may be

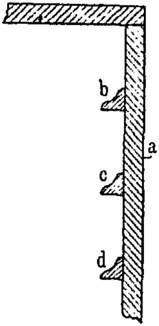


FIG. 13.

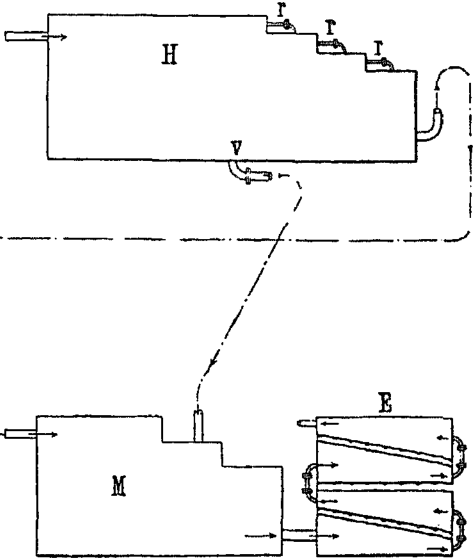


FIG. 14.

partitions into several intercommunicating compartments, each of which is by steps or continually lessened in section from the entrance to the exit of the gases. The gases, according to the above-mentioned principle, enter at the higher front wall, and go out at the lower back wall. This arrangement procures the advantage over the usual end chambers of making the gases travel a long way in a small space, which greatly promotes the complete working up of the SO_2 contained in the end gases in a very dilute form. Under abnormal circumstances, *e.g.* at extreme temperatures of the outer air, or during temporarily intensive or restricted work, the process can be regulated at will by a suitable setting of the slides in the connecting tubes *r r*, the number of which is arranged according to the width of the chamber. For a further regulation of the work a by-pass, *v*, is provided which is attached to the bottom of the main chamber, taking the sulphurous gas away from here and introducing it at will into the top of the intermediate chamber, or into the end chamber, or even into the Gay-Lussac tower. The principal object of this by-pass is the avoidance of the injurious consequences of temporary excessive separations in the chambers, by producing in the main chamber a good mixture of the gases through drawing them downwards, taking away the inactive SO_2 gases from the bottom and introducing them into the upper regions of the intermediate chamber, which may on their part be inactive on account of an excess of oxygen. Since the latter are not absorbed to any great extent in the Gay-Lussac towers, and also act corrosively, that by-pass causes, besides a uniform utilisation of the whole system, also a smaller consumption of nitre and less action on the apparatus. The periodical regulation of the by-pass, apart from slide-valves, is also attained by interposing a tower fed with cold chamber acid; by the quantity of that acid the upward tendency of the gases, and therefore also their quantity, can be regulated.

1914, these "step-chambers," together with the end chamber divided into compartments, are most suitable for mechanical burners, and allow of normal working even with most dilute gases, showing 10 to 11 per cent. oxygen in the exit-gas. Only one fan-blast is required at the end of the system, which essentially lessens the formation of dust in the furnaces, and simplifies the work, with a reduced consumption of nitre. The by-pass conduit produces very economical and regular working of the chambers.

Krantz (Ger. P. 283065) forms the bottom of the vitriol chambers in steps, each of which has an outlet for the acid. The inner margins of the steps project over their bottoms in such a way, that upon these a layer of acid not exceeding 2 in. is formed; this prevents damage to the bottoms from acid drops falling down, and causes a good cooling of the gases. The superior cooling by increasing the surface of chambers causes also better condensation of the acid fog before entering into the Gay-Lussac tower. Each step has its own outlet for the acid, so that this can be run off at various concentrations, between 50° and 60° Bé., and only part of the acid need be more highly concentrated in the Glover tower. This construction may also be arranged for existing chambers.

Mills, Ch. T. Packard, and Packard & Co. (B. P. 12067, 1913; U.S. P. 1112546; Fr. P. 492366) employ chambers in the shape of truncated pyramids or truncated cones, cooled from without by flowing water, so that the temperature can be kept constant at every season of the year. The gas coming from the Glover tower enters the first chamber at four evenly divided places, and goes out by an opening in the centre of the top; the same takes place on passing from one chamber to another. By the diminution of the horizontal sectional area of the chambers from the bottom upwards the density of the gases, which decreases through the formation of sulphuric acid, is again

Proposals for Diminishing the Chamber Space.

Page 651. J. A. Hart (Ger. P. 272984) describes an arrangement for causing a mutual action between liquids and gases or vapours, by dividing the gas into many small currents, directed tangentially to the curvature of the concave plane of conduit.

Producing an Acid Spray in the Chambers, in order to Improve the Mixture of the Chamber Gases.—G. K. Davis (B. P. 15459 of 1912) arranges in the chamber transverse shafts with agitating-blades, and divides each chamber by a partition into two compartments. The revolution of the blades causes the acid to be squirted over from one compartment into the other, and circulation is effected by an outside, water-cooled channel through which the acid goes back into the chamber. This arrangement admits of making the chamber more efficient than usual, and it may also be employed for denitration and for the absorption of nitrous vapours.

Page 656. *Falding's System of Acid-chambers.*—Hartmann (*Z. angew. Chem.*, 1912, p. 381) considers that system inferior to the tower systems, on account of requiring too much power for pumping the acid. Petersen (*ibid.*, p. 762) defends the system against that objection. Keppeler (*Jahresber. d. chem. Techn.*, 1912, p. 381) asserts that it has not been practically successful.

Falding and Cathcart (*J. Ind. Eng. Chem.*, 1913, p. 223) deduct the superior action of their high chambers from the special conduction of heat existing therein. The first chamber on that plan was started on 1st January 1907, at Vandergrift, succeeded by the plant of the Tennessee Copper Company at Copperhill (36 chambers), and many others. Experience has proved the following advantages of Falding's system over the gales. (5) Saving of wages in working.

R. Hoffmann, in *Chem. Zeit.*, 1913, p. 1271, describes the Falding plant at the Tennessee Copper Company's works. It produces per annum 140,000 tons sulphuric acid 60° Bé., from 400,000 tons poor copper ores, mostly pyrrhotite, with a little pyrites, which is smelted for matte in blast-furnaces. The Ducktown Sulphur, Copper, and Iron Company also works up the gases from the pyritic smelting, at present from 150,000 tons of ore containing 14 to 19, on the average 16 per cent. sulphur, in Falding chambers, obtaining therefrom 50,000 tons acid 60° Bé.

Tower Apparatus for the Manufacture of Sulphuric Acid.

Volberg (Ger. P. 265724) arranges the packing of towers, etc., in such manner that the single successive layers, *e.g.*, of fireclay cylinders, are out of line with those above and below them. Each cylinder is filled with coke or charcoal in such a way that there is always sufficient space for the gases to pass through. This avoids the otherwise unavoidable lack of uniformity in the channels for the gases.

Carmichael and Guillaume (B. P. 15679 of 1913) employ a series of vertical chambers, *i.e.* towers, which are in turn left empty and provided with packing, so that the gases, after passing a chamber tower, filled with packing, can extend again in the next, empty tower.

The Opl tower system, according to the *Alkali Inspector's Report for* 1912 (p. 12), had been introduced in a second English factory, where it did satisfactory work.

Opl (*Chem. Ind.*, 1914, p. 523) states that in his system usually six towers are employed, the three first forming sulphuric acid similar to Glover towers, and the three last retaining the nitrous gases in strong sulphuric acid, like Gay-Lussac towers.

through an overflow is fed into the first tower; the acid from the fifth tower goes into the second, and that from the fourth tower into the third. Finally all the acids go into the first tower, and from this through coolers into store-tanks. The acids supplied to the three last towers are also cooled, in order to carry away the injurious heat of reaction. Owing to the better utilisation of the space, the acid-forming process requires only about twenty minutes, against four to six hours in the chambers. The reacting space is about one-tenth of that in the chambers. *For the daily production of* 18 *tons sulphuric acid* of 60° Bé., six towers of 3 m. × 3 m. section and 12 m. high are required; that production requires 12 tons pyrites, 4 kilowatt power, 4000 cb.m. air compressed to 2 atmospheres, 160 kg. nitric acid 36° Bé., about 300 cb.m. cooling-water, and three men's work per shift (inclusive of the pyrites-burners). The cost of building a simple tower system, inclusive of sheds and furnaces, is 224,000 Austrian kroner, against 371,000 kroner for an ordinary chamber system doing the same amount of work. According to Huntingdon, Heberlein & Co., thirty such systems were then being worked or in course of erection.

Other Tower Processes.—The name "Witney" on p. 1571 should be spelt "Whitney."

The German patent for the invention of Petersen, mentioned on p. 694 of our text as being applied for on 28th December 1905, according to *Z. angew. Chem.*, 1912, p. 456, has not been granted.

Düron (B. P. 2408 of 1913; Ger. P. 267138; Fr. P. 453733; Austr. P. appl. A, No. 823, 1913) describes a tower system for the manufacture of sulphuric acid, consisting of one or several towers for concentration, denitrification, reaction, and absorption. The reaction towers are fed with nitric acid and water, and with their own acid; the absorbing towers (Gay-Lussac only five towers. The hot burner-gases enter into the first tower at the bottom by a tangentially arranged inlet, whereby whirls are produced, and the gases, in spite of the large sectional area of the towers, are evenly distributed. Here the sulphuric acid running down is concentrated at least to 60° Bé. The gases leave this concentrating tower through three branch conduits at the top, and pass into the second, the Glover tower, which is fed with the nitrous vitriol obtained from the two Gay-Lussac towers (Nos. 5 and 6) and the acid obtained from the third and fourth towers; here pure, denitrated sulphuric acid of 57° Bé. is formed which goes into the first tower and is concentrated there. Towers Nos. 5 and 6 work exactly like Gay-Lussac towers. The gases coming out of these towers, which contain no more SO_2, may issue immediately or through a sand-filter into the outer air. Every tower is fed by itself with previously cooled acid, so that they work independently of one another; the concentration of the acid formed here is kept at 55° Bé., and it is passed on to the Glover tower. Only two of these six towers are provided with a roof. The towers are conical, like factory chimneys, and, owing to their construction, they possess great stability, so that they require no supporting frame.

Burckhardt (B. P. 29568, 1912; Ger. P. 259576; Fr. P. 452682) passes the hot burner-gas upwards in a tower, containing a number of superposed pans, filled with dilute sulphuric acid, whereby this acid is concentrated and the gases are cooled and saturated with an aqueous vapour. They then pass over a series of pans, filled with nitrous vitriol; from these the sulphuric acid formed is run into a dividing apparatus which delivers them to the first tower. The remaining gases go through a Gay-Lussac tower. According to his Ger. P. 254921, he replaces the pan-shaped vessels by channels, filled with packing materials, and divided by walls dipping into a shallow towers, partially or entirely filled with packing materials, with alternately narrower and wider interstices, over which nitrous vitriol runs down. Between the two last towers one or more empty towers may be placed, in order to diminish the velocity of the gases.

Steuber & Co. (D. R. G.-M. No. 541504) line the towers with stones, the inner faces of which are made slanting. This diverts the running-down acid towards the interior of the tower, so that the cemented joints of the stones are not hit by it, and also prevents the acid from getting out.

J. Mackenzie (B. P. 19084, 1913) employs a series of long tunnels, made of acid-resisting bricks or blocks, in which are placed lead spouts lined with acid-proof bricks, of such depth that an hydraulic lute is formed by the acid. The tunnels are in suitable intervals provided with tuyeres for introducing acid, squirted in by centrifugal pumps or otherwise, preferably taken from the same tunnel, whereby the whole tunnel is filled with a strong rain of acid through which the gases must pass, while fresh sulphuric acid is made and condensed.

Schliebs (Ger. P. 287589) places in a tower system behind single or all towers an "equaliser," by which in case of need the gases may be reconducted to the towers in circular motion.

According to U.S. P. 1151294 of Schliebs, the reacting gases are passed through a succession of towers, with a separator interposed between adjacent series, and a portion of the uncondensed gases is returned from each separator, through a conduct furnished with draught-producing means, to the preceding series of towers.

Fr. Curtius & Co. (B. P. 28550, 1913; Ger. P. 287784) pass the gases in the cold state into the tower system. Either the first tower, from which all the acid produced is taken, is fed with a comparatively small quantity of nitric acid or nitrous produced is taken, and which is made considerably larger than hitherto usual, may be packed with coke, which is much cheaper and has a much greater surface than rings or stones. In a plant of six towers, all the acid produced in towers Nos. 2 to 4 is put on to tower No. 1, where it is denitrated and runs off as acid of 60° Bé. Towers 5 and 6 act as Gay-Lussac towers. The nitrous vitriol from tower 6 goes to tower 5, and together with the acid from this tower to tower 2, or else directly from tower 6 to tower 2.

U. Wedge (U.S. P. 1104500) passes the burner-gases by means of an exhauster, after they have gone through the Glover tower, through several rows of lead towers of about 10 superficial ft. section and 70 ft. high, alternately entering at the top or at the bottom, whereby they are well mixed and produce a great deal of sulphuric acid. The steam present in excess is used up so quickly that the gases, after leaving the last tower, may be still utilised in ordinary chambers for the production of sulphuric acid. In a plant constructed in this way the gases coming out of the burners showed about 620°, on coming out of the Glover, 135°; after passing through eight rows of nine towers each, altogether seventy-two towers, their temperature had gone down to 88°.

The Metallbank und Metallurgische Gesellschaft A. G. and Hans Klencke (Ger. P. 284995) pass the gases in one or in all the towers from the top downwards, whereby the reaction is increased.

Littmann (Ger. P. 281005) employs a series of towers filled with pipes, and provided in several places one above the other with branching-off outlet-tubes, connected with the tube leading from the bottom of one tower to the top of the next tower. According to his Ger. P. 281537, the pipe-towers are to be shaped in steps; the back wall may be smooth, the steps being the steps, ring-shaped vessels are placed containing cooling-water, which in case of need may be made to run over the sides of the step-tower.

Hartmann (Ger. P. 282747) places between the reaction towers and the Gay-Lussac tower a tower filled with coke, stoneware packing, etc., and in case of need fed with sulphuric acid, for the purpose of condensing the acid fogs. According to the Ger. P. 284636 of Hartmann and Benker, they employ six towers; the first forms with the fifth, and the second with the last tower, closed rings for feeding with acid. The towers are packed with fireclay materials, *e.g.*, Glover rings. Towers 1, 2, and 3 serve for producing acid; the acid fog carried away by the gases is partially retained in tower 4; tower 5 serves as the principal Gay-Lussac. The above-described crossway connection of tower 1 with 5, and tower 2 with 6, causes the strongly nitrous acid from 5 to get on to 1, and thus produces a strong formation of sulphuric acid.

In *Eng. and Min. J.*, ci. p. 10 (1916), experiments are described for producing sulphuric acid by passing the gases through a spiral of lead, instead of chambers or towers, retaining the Glover and Gay-Lussac towers. In such a spiral the gases are very intimately mixed, and the most suitable temperature is easily attained by air- or water-cooling. Up to the present only experiments on a small scale have been made with this process.

The same process is described by Waggaman in U.S. Dept. Agric. Bull. No. 283, Sept. 28, 1915 (extr. in *J. Soc. Chem. Ind.*, 1916, p. 42); his U.S. P. is No. 1185029.

Steffanson (*Chem. News*, 1915, cxii. p. 255) discusses the tower systems for the manufacture of acid sulphites.

CHAMBER FITTINGS.

of nitric acid to the Glover tower by connecting the apparatus with the chamber thermometer in such a way, that on the rise of the temperature in the chamber the feeding-apparatus is automatically throttled, and on the falling of the temperature again opened.

Page 720. The supply of nitre to the chambers, by introducing an aqueous solution of sodium nitrate into the first chamber in the shape of a spray, according to the *Fiftieth Report of the Alkali Inspector* (for 1913), page 133, has answered very well, especially owing to the regularity and rapid adjusting of the feed. The drawback caused by some sodium sulphate dissolving in the chamber acid is of no importance, if the acid is used for the manufacture of fertilisers.

E. W. Kauffmann found the supply of nitre to the chambers in this form at various French works, and applies this way himself in such cases, where a slight contamination by sodium sulphate is of no consequence. By this proceeding a saving of 0·45 mark per ton of chamber acid is effected.

Howard (U.S. P. 1151103) interposes in the flue leading from the burners to the Glover tower a closed apparatus, provided with an agitating apparatus, for decomposing the mixture of nitre and sulphuric acid. This mixture is first introduced into a second apparatus, placed above the first, also provided with an agitator, and runs out of this through a pipe, containing a screw-carrier, which delivers it in an even manner to the lower apparatus, in which ultimately remains neutral sodium sulphate of commercial quality.

Page 722. *Employment of Nitrous Gases from Oxidising Operations.*—Hedenström (*Chem. Zeit.*, 1914, p. 803) draws attention to the fact that nitrous gases, obtained in the oxida-

p. 125.

Page 722. *Supply of Steam for the Acid-chambers.*—The placing of steam-boilers over the sulphur or pyrites burners, which had been abandoned everywhere, is reintroduced in the Ger. P. 263941 of Cellarius, mentioned *suprà*, p. 200.

Page 735. *Spray-producers for the Acid-chambers.*—The German patents for Rabe's spray-producers mentioned in the text are Nos. 237561 and 246240.

A spray-producer, made of glass, and sold by the name of "Skorpion," is recommended as being very simply constructed and producing a hardly visible veil of water, without the formation of drops. It is worked at from 3 to 8 atm. pressure.

Poley's spray-producer, mentioned in our text, p. 1572, is protected in Germany by D. R. G. M., No. 3139, and shown in Fig. 15. For acid-chambers it is always made of glass. The tube, introduced into the chamber wall by a rubber stopper, has inside a conically-shaped end; by the glass or hard-lead spiral placed in the contracted part, the liquid is caused to assume a whirling motion. The junction with the water-conduit is made by an ebonite screw, with rubber rings inside. This apparatus sprays at a pressure of 4 atm. in the water-conduit from 20 to 24 litres of water per hour. Other details are given in the text. The taking out of this apparatus for the sake of controlling is much easier than in the case of platinum spray-producers.

The Harkortsche Bergwerke und Chemische Fabriken (Ger. P. 275388) convert the water into spray by a glass vessel, provided with a central outlet opening, and with grooves running from the top downwards in curved paths; a glass

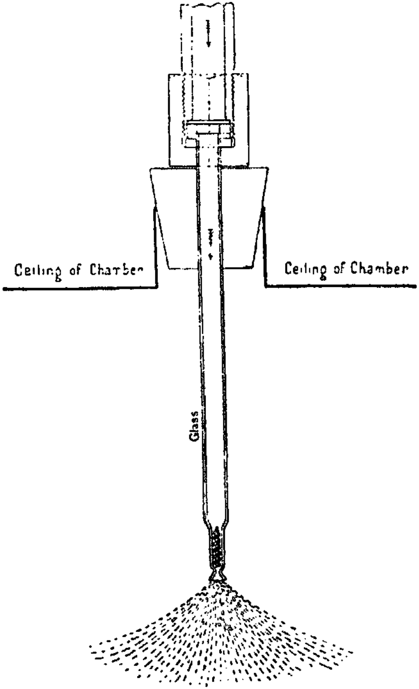


FIG. 15.

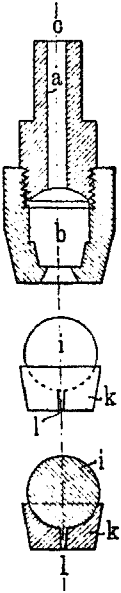


FIG. 16.

regulation of the work of the spray-producers. It consists of a balance, into which acid flows from the chamber walls; if the density of the acid is above or below the normal, the balance goes out of level and starts a lever by which a valve in the water-conduits is correspondingly set. One form of this apparatus consists in a lever, with a counter-weight, on which is suspended a cup taking up the acid, fitted with an in turn start two levers by which the water-valve is worked by means of an excentric. The specification describes still other forms of the apparatus.

Schüphaus (*Metall und Erz*, 1915, p. 504; *Z. angew. Chem.*, 1916, ii. p. 171) discusses the advantages of supplying the acid-chambers with water-sprays. The water is best pre-heated to 60° to 70°.

Haughton's Metallic Packing Co., London, sell an acid-spray producer of new shape for application in vitriol chambers, in connection with a centrifugal pump made of acid-proof material, which is easily and cheaply applied to existing chambers.

Sache employs spray-producers with glass points; the middle part is made of lead, and the supply-pipe of bronze.

Other forms of spray-producers for vitriol chambers are described by Düron (Ger. P. 221779); General Chemical Co. (U.S. P. 1032657); Parent (Fr. P. 462349); D. H. Thomas (B. P. 19867, 1912).

Nagel (*J. Soc. Chem. Ind.*, 1914, p. 522) discusses the introduction of water in the form of spray into vitriol chambers. Care should be taken that all the gas for the chambers is forced through the tuyeres as well, which is attained by connecting the pipe leading from the Glover tower into the first chamber, with the entrance opening off the steam spray-producer. The bottom part of the casing for the blast should be made wider than the other parts, and here the gas should be cooled down to 65° by a tubular air- or water-cooler. The gases should go from the Glover tower through the spray-producer into a small chamber, and from this through two reaction towers into the Gay-Lussac tower. The gas preferably enters into the apparatus at atmospheric pressure, so that the blast acts only as a mixing agent. In this way whilst formerly 0·7 to 0·8 kg. nitric acid was required. The "Union" feeds its chambers only during the warm season with water-spray, but in winter time with steam.

According to the Fiftieth Report of the Alkali Inspector (for 1913, p. 133), seven factories of the East-English district had introduced the exclusive application of sprayed water, in lieu of steam, for the vitriol chambers, in all cases with thoroughly satisfactory results. The chamber space required in this case is much smaller than when working with steam, since it is possible to work at lower and more easily controlled temperatures. In one case they had got down to 11·4 cub. ft. of chamber space for burning 1 lb. of sulphur per diem, and that set had then already for sixteen months worked quite smoothly, with an average contents of 0·78 (*in maximo* 1·1) grains of acid in the gas.

Supply of Air to the Vitriol Chambers.

Heinz (U.S. P. 1057149; Ger. P. 286972) forces air, to the extent of 6 to 8 per cent. above that required for oxidising the SO_2, into the pipes taking the burner-gas to the chambers, and keeps up that excess during the whole process, in order to produce a uniform pressure and motion of the gases in the chambers.

M'Farland and the General Electric Co., New York (U.S. P. 1112424), employ for the production and automatic regulation of the draught in vitriol chambers a mechanical arrangement, placed on the exit-pipe of the last chamber, which produces the draught, without its inside mechanical parts coming into contact with the acid-containing exit-gases, as is the case with ordinary exhausters. Compressed air is forced by an electromotor through a narrow opening into a correspondingly shaped branch tube of the chimney, and in well-known manner carries along manner that a non-attachable covering is formed on the fan-blast.

Page 744. *Injectors for Producing the Draught in Vitriol Chambers.*—It is mentioned in the text that porcelain injectors crack very easily; but those constructed by the Vereinigte Tonwarenwerke at Charlottenburg from stoneware stand very well. Still, the easily happening obstructions of injectors are a great impediment to their employment for acid-chambers.

Page 755. *Fans for Producing the Draught in Vitriol Chambers.*—The B. P. 15293 of 1913, of the British Thomson-Houston Co. (for the General Electric Co. at Schenectady, U.S.A.) describes a centrifugal fan with controllable speed.

Kestner Fans.—According to a communication from the firm Paul Kestner, of 181 Queen Victoria Street, London, E.C., in the year 1912 upwards of 1000 of their hard-lead fans were working all over the world. It is specially pointed out that they are very durable, and require very little power for driving. They are now made for temperatures up to 125° and working-pressures up to 250 mm., and are employed for acid-chambers and tower systems, and in the concentration of sulphuric acid by Kessler's process (*vide* our text, pp. 1191 *et seq.*).

Methods for Judging of the Draught in Vitriol Chambers.

Kuhlmann fils (*Année Indust.*, 1878, p. 67; *Chem. Ind.*, 1878, p. 137) produces coloured vapours at the foot of a chimney, and notices the time which they require for coming out at the top. A similar process (production of a fog of sulphuric-acid vapours) had been already employed by Fletcher.

K. Walter (communication to the Author) employs a small bromine, the pinchcock is opened, and the number of seconds is noticed which the bromine vapour takes to travel through the glass tube of a metre's length. This small apparatus is very suitable for very small amounts of draught, *e.g.*, in muffle-furnaces for the production of sodium sulphate.

Page 776. *Anemometers.*—A. König's anemometer is on the same principle as that of Seger, described in the text, but more easily handled, as the communicating tubes are concentrically arranged.

Verbeek (*Chem. Zeit.*, 1913, pp. 1338 and 1361) discusses at length the measurement of the over- and under-pressure of gases (the draught), and describes two apparatus which avoid the drawbacks of König's apparatus, viz., the "precision differential manometer" (Ger. R. G. M. 560918) and the "precision controlling manometer" (Ger. R. G. M. 559644).

CHAPTER VI

THE RECOVERY OF THE NITROGEN COMPOUNDS

Packing of Gay-Lussac Towers.

Page 793. The packing described by Green and the Huncoat Plastic Brick and Terracotta Co. for Glover towers in B. P. 28004 of 1910, is also applicable for Gay-Lussac towers.

The Nitrogen Products and Carbide Co., Ltd., and H. Nielsen (B. P. 26269 of 1913; Fr. P. 465937) describe a filling material for absorbing-, reaction-, mixing-, and cooling-towers, comprising three or more arms or blades radiating from a central boss. The blades may be either straight or helical, and smooth or corrugated, and the central boss may be with or without a central hole. These pieces can be made cheaply by pressing a plastic material through a die.

The Ribbertsche Braunkohlen- und Tonwerke (D. R. G. M. No. 573710) provide the packing-blocks on their whole surface with grooves and projections like dragons' teeth.

Raschig (B. P. 6288 of 1914; Ger. Ps. 286122 and 292622; U.S. P. 1141266; *J. Gasbeleucht.*, 1916, p. 597) packs reaction- or absorbing-towers with small cylinders which are simply dropped into the towers, and are therefore heaped up in these in an irregular manner. These cylinders are about as wide as high, from 15 to 50 mm., and about 1 mm. thickness of walls. They are easy to make, offer but little resistance to the gas-current, and yet compel it to frequently change its direction. They are made of metallic sheets cut into rectangular pieces which are

Apparatur, 1915, p. 247), every cubic metre of tower-space contains 55,000 Raschig rings, leaving 92 per cent. of the space free for the transit of the gases.

The Accrington Brick and Tile Co., Ltd., and S. Middleton (B. P. 8152 of 1915) furnish Glover, Gay-Lussac, and like towers with channelled packing-blocks, arranged so as to produce long, narrow, inclined passages. These earthenware blocks are easy to make, and comparatively few of them are required; they may be used in an upright or in an inverted and reversed position. If the blocks are placed end to end, and alternate blocks of each layer are reversed, or if they are laid on the top of another, while the alternate blocks are reversed, a wall-like tier is produced through which runs a series of continuous, zigzag channels. The tower can be completely filled with these tiers, in such a way that they are independent of one another.

Mescher (Ger. P. 259764) employs spouts, arranged in turns on one or the other side of perforated plates, which force the gases or vapours to sudden changes of direction, leaving the substances condensed behind on the faces of the preceding plate.

Kubierschki (Ger. P. 259362) employs wire spirals made up into plates. In this way upwards of 100 superficial metres can be placed in 1 cb.m. of space.

Other proposals for packing reaction-towers will be described in connection with the Glover towers. Volberg's proposal is mentioned, *suprà*, p. 217.

Bithell and Beck (B. P. 28743 of 1913) describe Gay-Lussac and Glover towers, consisting of several superposed parts, every one of which has a chamber with an upright tube, over which is put a cover with lateral openings. The single parts of this column are connected by pipes. The gases enter from below. This construction avoids the drawback of towers packed with tubes, etc., forming throughgoing channels which are traversed by the gases too quickly.

of chambers, containing from 20 to 30 or 50 per cent. of the total volume of the chambers, in which the nitrogen oxides are successively exposed to contact with acids of sp. gr. 1·21 to 1·26; 1·07 to 1·21; and 1·00 to 1·10.

Moritz (Fr. P. 462877) provides absorbing- or reaction-towers with vertical or horizontal partitions, so that the liquid can freely run down, but the gases must take a circuitous route. The partitions are kept in their places by the packing.

Höfling (Ger. P. 272608) arranges within the towers the packing in the way of a winding staircase, whereby the gases are compelled to overcome a great friction and mixing resistance, and also in their revolutions to separate the liquid particles. If the acid is run down from the top and heating gases are passed in below, the tower may act as an acid-concentrator. According to his Ger. P. 281135, he employs pieces of tubing, provided with holes and diaphragms, built up in the towers in such a way that throughgoing channels are avoided.

Schlossberg (Ger. P. 258683 and Ger. P. appl. Sch. No. 43938) works up quartzite, colloidal silica, and lime with a flux of glass or ground bricks into a mass from which stones are moulded; these are treated with hydrofluosilicic or hydrochloric acid, the lime salts formed are removed by washing, and the stones are burned at 800° to 1200° up to sintering.

Nielsen (*Chem. Trade J.*, liv. pp. 565 and 621) discusses at length the materials and moulded bodies employed for packing absorbing- and reaction-towers. Camillo Guttmann (*ibid.*, p. 671) makes critical remarks upon this. The discussion is continued by Nielsen (lv. p. 97) and Guttmann (p. 98).

Schobner (*Tonindustrie Zeit.*, 1913, p. 1429) and Ludwig (*Chem. Apparatur*, 1914, p. 271) discuss the various packings for reaction-towers without adducing anything new.

distance pieces. For circular towers, the bricks are arc-shaped.

The Alkali Inspectors' Report for 1915 makes the following statements on the packing of Gay-Lussac towers in the United Kingdom :—

Description of packing.	Balls.	Bricks.	Coke.	Glass.	Lunge-Rohrmann tiles.	Rings.	Tiles.	Bricks and tiles.	Rings and coke.	Rings and tiles.	Bricks or tiles and coke.	Total.
Number of towers .	1	53	269	48	3	25	17	10	8	4	7	440
Per 1000 towers .	2	120	611	98	7	57	39	23	18	9	16	1000

Page 795. *Accidents through Poisonous Gases in repacking Gay-Lussac Towers.*—This matter is also mentioned in the *Thirty-Third Annual Report of the Inspector of Alkali Works* (for the year 1896), and in the Forty-Third Report (for 1906). The Forty-Ninth Report (for 1912), p. 12, enumerates the precautions which should be taken in this operation.

(1) Washing the tower with strong sulphuric acid, to remove any nitrous vitriol prior to washing with water and steaming.

(2) The maintenance of a downward draught, to remove as directly as possible any gases present from the men engaged at the work.

(3) The use of a "safety pipe," as required by the Special Rules of the United Alkali Co., Ltd. This safety pipe consists of a metal funnel, the stem of which acts as inlet-pipe. It fits with a pneumatic pad against the face (this pad can readily be blown up for use, being similar to that used in dentistry in

Lussac towers, Chance carbonators, etc.

Respirators for men dealing with dangerous gases are described and illustrated in *Chem. Ind.*, No. 14; *Beilage*, pp. 30 and 31.

Schubert (*Chem. Zeit. Rep.*, 1912, p. 26) points at the frequency and dangerous character of poisoning by nitrous vapours, which frequently only appears several hours after breathing the gas. He recommends a series of precautionary measures to be taken at the factories, and the use of dilute liquor ammoniæ for moistening pieces of cloth to be kept in front of the mouth and nose.

Page 805. *Distribution of the Acid on the Towers.*—Pauling (Ger. P. 242515) employs a reservoir connected on one side with a filling apparatus acting from time to time, on the other side with an apparatus dividing the liquid into a certain series of jets, *e.g.*, in the shape of a veil or a bell. The dimensions and performances of the reservoir, and those of the filling and emptying apparatus, are arranged in such manner that the veil formed by the running-out liquid is gradually enlarged, attaining a maximum at the highest level of the liquid in the reservoir, and gradually diminishing up to the complete emptying of the reservoir. The arrangement for delivering the liquid may be provided with one or several outlets, so that a uniform division of the liquid is attained, whatever the section of the body to be fed may be, whether square or longitudinal, or otherwise.

William Mason (*Chem. Zeit.*, 1914, p. 800) describes an overflow-distributor for acid towers, of the type of a spinning-wheel, and a new form of outside and inside coolers.

Noll (Ger. P. 276665) describes an apparatus for mixing liquids with gases, consisting of a ring-tube with outlets for the liquid surrounding the gas-pipe which enters into the contracts to a rod, on which the liquid contained in the plate freely runs down, influencing the diameter of the liquid bell solely by its quantity. The periodical change of the quantity of liquid is produced by a siphon, the descending branch of which is connected with a closed vessel containing outlets with the same resistance for the single branch conduits, which may be arranged in groups. The periodical siphoning automatically fills all the branch conduits, as they have all the same resistance, and washes away any impurities remaining at the conclusion of the siphoning during the retardation of the current at the next siphoning, so that no special supervision is required.

Pumping of the Acid.

Page 822. Nagelschmidt (Ger. P. 279074) avoids the jerks and splashes in pumping by applying an intermediate pipe between the lower acid-reservoir and the "emulsioner," and a pulsometer between the emulsioner and the top reservoir.

Moritz (Fr. P. 441304) places the pumps, made of an acid-resisting material, within the acid contained in the reservoir, by which means many troubles otherwise occurring in the pumping of acid are stated to be avoided.

Ferraris (B. P. 4482, 1914; Fr. P. 457936) interposes in pumping acids a layer of mercury or of some suitable oil between the pump-piston and the acid, which protects the piston from corrosion.

The "Mammoth-pump" of the engineering works A. Borsig, at Tegel, near Berlin, is specially recommended for pumping acids, as it has no valves or other moving parts (described in *Chem. Zeit.*, 1914, p. 274).

Haughton's Patent Metallic Packing Co., Ltd., 30 St Mary-at-Hill, London, sells centrifugal pumps made of a material completely resisting the attack of acids.

p. 844, the B. P. 10866, 1910; Ger. P. appl. T., No. 16457.

According to their B. P. 16611, 1912, the washing with alkali may be left out if the washing with water has been well done.

According to their B. P. 9461, 1911; U.S. P. 1068021; Ger. P. 268815, they remove from the gases going out of the Gay-Lussac tower first the sulphur acids, by treating them with alkaline-earth carbonate in lumps, and then absorb the nitrous gases by solutions of caustic or carbonated alkali, with formation of sodium nitrate and nitrite. This treatment takes place in towers or scrubbers, which are either left empty (in which case the alkaline liquids are introduced in the form of spray) or filled with packing materials. Into the first tower air is injected in order to oxidise the NO. The solutions of nitrate and nitrite obtained are sprayed into the vitriol chambers. They also pass these gases first through earth-alkaline carbonates, in order to retain any sulphuric acid carried away. According to their Ger. P. 277324, the sulphuric acid carried away is retained by washing with water, in lieu of alkaline earths.

Page 844. *Testing the Exit-gases for Acids.*—Henz (*Z. angew. Chem.*, 1905, p. 2002) recommends for this purpose an absorbing vessel, shown in Fig. 17. The vessel is charged with 25 c.c. normal soda solution; a quantity of gas, measured by means of an aspirator, consisting of a large stoneware jar filled with water, is passed through; the liquid is poured out (without rinsing the absorbing-vessel) into a beaker, retitrated with normal acid until the colour of the indicator changes, poured back into the vessel, again blown into the beaker, and the titration is finished.

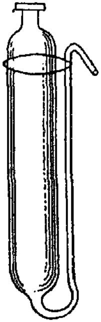


FIG. 17.

Page 845. *Various Methods for Recovering the* pure nitrates.

The same (Ger. Ps. 233967 and 233982; Fr. P. 412788) absorb the nitrous gases by bases suspended in a finely divided form, without towers.

Wachtel (*Dingl. polyt. J.*, ccxlv. p. 517) proposes driving the exit-gases through a red-hot iron or fireclay retort, filled with iron borings. Here, he supposes, the nitrous vapours will be reduced to ammonia, which is then absorbed by hydrochloric or nitric acid.

Mechanical washers for the recovery of nitrous gases leaving the last chamber, according to the Alkali Inspectors' Report for 1915 (quoted from *Chem. Trade J.*, 1916, p. 284), had been successfully introduced in one works, and were on the eve of introduction into others. They have the advantage over Gay-Lussac towers that there is no obstipation and repacking.

Glover Towers.

Page 867. Quinan (U.S. P. 699011) places between the pyrites-burners and the Glover tower a "mixing chamber," followed by an ascending flue, the bottom of which is formed of shallow troughs of Volvic lava. Each trough is by a flange at its front end connected with the next lower trough, and the Glover acid flows along this step-channel into the mixing chamber.

Packing of Glover Towers.

Page 869. Cast silicon is employed for the purpose by F. T. Tone and the Carborundum Company (*Metall. and Chem. Eng.*, 1913, p. 103).

Page 875. Scherffenberg's packing-bricks, mentioned in the text, are sold by the name of "fluted rhombohedric tower-packing." According to information received in September sides of which are bent in towards the centre. This slight deformation prevents the tetrahedra from touching in more than two points; moreover, some liquid is retained at every curved edge, which promotes the absorbing action. Fig. 18 shows these tetrahedra. Part of the gas rushing upwards must pass through the wire-netting, and thus gets into intimate contact with the adhering liquid. Another part rises upwards at the side surfaces of the tetrahedra, and there gets into action. These bodies may be thrown into the tower without being regularly placed. They have a very slight weight, and occupy only from 1 to 3 per cent. of the tower space, with great acting surface. For Gay-Lussac and Glover towers they are made of lead-coated iron wire (preferably produced by Schoop's process of converting lead into dust); for the conversion of nitric acid from nitrous gases they are made of aluminium wire.

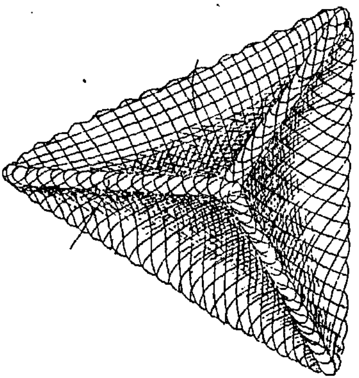


FIG. 18.

Höfling (Ger. P. 281135) packs Glover towers, etc, with pieces of tubing, provided with perforations and partitions, the Glover tower is almost instantaneous; already at 3 ft. 3 in. below the exit-pipe it had proceeded to its maximum. But it would be wrong to ascribe general validity to that observation; the result quoted is probably only attained with greatly diluted acid and very hot gases. Although no doubt the principal denitrating work is done in the top part of the tower, a *complete* denitration will require a depth of 10 ft. or upwards, apart from the requirements for performing the concentrating work.

For the denitration of *poor* gases, *e.g.* those produced in the roasting of lead ores, the Aktien-Gesellschaft für Bergbau, Blei- und Zinkfabrikation (Ger. P. 253493) supply the Glover tower with stronger gases, especially those obtained by roasting zinc-blende, iron pyrites, copper pyrites, etc., and mix the acid gases thereby formed with the dilute SO_2 gases to be oxidised.

The Alkali Inspectors' Report for 1915 (quoted from *Chem. Trade J.*, 1916, p. 284) makes the following statements on the packing of Glover towers in the United Kingdom:—

Description of packing.	Bricks.	Flints.	Rings.	Tiles.	Bricks and flints.	Bricks or tiles and rings.	Bricks and tiles.	Total.
Number of towers .	127	130	23	8	28	16	6	338
Per 1000 towers . .	376	385	68	23	83	47	18	1000

Page 893. *Testing of Glover Tower Acid.*—The acid running out of the tower is tested for its strength (which should be between sp. gr. 1·71 and 1·75); for its temperature (if it is to be immediately pumped up on to the Gay-Lussac tower); and

Page 901. *Temperature of the Gases entering into the Glover Tower.*—It is not necessary for the denitrating action of the Glover tower that the gases passed into it should have a high temperature. In some factories the concentrating work is entirely done by pans placed on the gas flues and the dust-chambers, which, of course, greatly reduces the temperature of the gases, without any detriment to the denitration. In a special case observed by me, where the gases pass into a small "plate-column" with a temperature of 90° and come out with 60°, during their short transit four-fifths of the denitrating work was done in that column of 3 ft. 3 in. height. In this case it was important to perform the denitration at as low a temperature as possible, because the burner-gases, produced from spent oxide of gas works, contained considerable quantities of ammonia, which at higher temperatures would act upon the nitrogen oxides and form elementary nitrogen.

Other Methods for the Denitration of Nitrous Vitriol.

Page 903. Parent (Fr. P. 449035) introduces cold gas, containing nitrous acid, from the last chamber of the Gay-Lussac tower continuously by spray-producers into the first chamber, or into small towers, not containing any packing between the chambers. This process is stated to effect a higher concentration of the chamber acid, a better circulation of the gas, a smaller consumption of nitric acid, and an increased production of sulphuric acid.

CHAPTER VII

THE CHAMBER PROCESS

Page 912. *Supply of Air.*—N. L. Heinz (U.S. P. 1057149) prescribes mixing the steam, the nitrous and sulphurous gas, with regulated quantities of air in various places in such a way that the gas current in the chambers keeps at an even pressure, since the quantity of oxygen contained in the air introduced is equal to that consumed by the reaction of the gases.

Page 973. *Escape of Acids in the Exit-gases of Sulphuric Acid Works.*—The British Alkali Inspector's Reports show the following average escapes, calculated in grains of SO_3 per cubic foot:—

Year.	In England and Ireland.	In Scotland.
1910	1·178	...
1911	1·153	...
1912	1·189	1·15
1913	1·182	0·99
1914	1·192	...

The number of works inspected in the year 1913 in England and Ireland was 236; in Scotland, 34.

Page 986. *Absorption of Nitric Oxide in Gas Analyses.*—According to Divers (*J. Soc. Chem. Ind.*, 1902, p. 1492), the absorption of NO is very easily effected by a concentrated alkaline solution of sulphites, say: 40 g. Na_2SO_3+4 g. KOH, dissolved in 200 c.c. water.

Baudisch and Klinger (*Ber.*, 1912, p. 3231) pass the gas

NO, one-fifth to the oxygen consumed for its oxidation: $4NO + O_2 = 2N_2O_3$. At the end of the experiments there must be still some free oxygen in the pipette.

Nitrogen protoxide, N_2O, occurs in small quantities in the exit-gases from the Gay-Lussac tower, and has been estimated in these by Inglis, as mentioned in our text, p. 953, where the analytic methods used by him are described. Other methods for the estimation of N_2O are described on p. 581. Its estimation alongside of NO is described by Moser (*Z. anal. Chem.*, 1911, p. 401), who absorbs the NO by potassium permanganate, or adds to the gases hydrogen peroxide and titrates the nitric acid formed; by Knorre and Arndt (*Ber.*, 1909, p. 2136); by Pollak (Treadwell, *Quant. Anal.*, 4th ed., p. 597).

Excess of Oxygen in the Exit-gases.—Pérégrin (*J. Soc. Chem. Ind.*, 1916, p. 1216) describes a registering apparatus for this purpose.

Theory of the Vitriol-chamber Process.

Page 1038. Briner and Kühne (*Comptes rend.*, 1913, clvii. p. 443) made some experiments in order to clear up the theory of the vitriol-chamber process. If dry, pure sulphur dioxide and nitrogen peroxide are conducted on to the bottom of a glass vessel, the lower half of which is immersed in a bath, kept at 60°, a white deposit of pure sulphur trioxide is formed on the walls of the upper, colder parts of the vessel. This proves that nitrogen peroxide can oxidise sulphur dioxide directly to SO_3. The authors believe that the reaction in the vitriol chamber goes on principally in the gaseous phase. The oxidation of SO_2 is essentially hastened by the water introduced into the chamber, because this water combines with the SO_3 formed, and removes it from the gaseous phase. According to their opinion, the formation of sulpho-nitro compounds within the lead chamber takes place only if in obtained by three of his co-operators on the chamber process, of which we here give an extract. Heymann introduced into an apparatus, containing nitrogen, oxygen, and a quantity of nitrogen oxides sufficient for the formation of sulphuric acid, a quantitative mixture of SO_2, oxygen and steam in the proportion required for forming sulphuric acid, of a certain concentration, obtained by allowing sulphuric acids of various concentrations to drop into an electrolytically heated furnace filled with bits of porcelain (which is minutely described in the original). He found that it was not possible, as he had hoped, to continue the experiments at will with a certain quantity of nitrous gases; the formation of sulphuric acid, which in the beginning went on very vividly, ceased after from two to three hours. From the nitrous gases considerable quantities of nitrogen protoxide were formed, perhaps even elementary nitrogen, incomparably more quickly than in a well-conducted vitriol chamber, although the total proportions of the reacting gases were relatively the same. The cause of this difference is probably this: that in the actual working of the vitriol chambers the water required for the reaction is introduced *gradatim*, whilst in Heymann's experiments the quantity of water introduced from the first corresponded to that ultimately contained in the sulphuric acid formed. In the fact that in technical work such a large production of N_2O does not take place, he sees an important argument for the theory according to which in the first instance nitroso-sulphuric acid is formed, which only subsequently is decomposed by water into sulphuric acid, NO and NO_2. If the total quantity of water enters from the first into the reaction, the conditions are given for the formation of nitrogen protoxide. These experiments show that it must be very important for working on the large scale not to introduce too much steam into the chamber all at once; also that it is very important for a good

(*J. Soc. Chem. Ind.*, 1904, pp. 642 *et seq.*; our text, p. 955) on the large scale, where the proportion of nitrogen protoxide was still much less.

In order to clear up the divergence between the results obtained by Inglis and Heymann, Hempel caused Johannes Richter to make experiments on the methods for estimating the nitrogen protoxide in gaseous mixtures of known composition. Heymann had estimated the N_2O after absorbing the higher nitrogen oxides by caustic-soda solution and sulphuric acid, Inglis by completely liquefying the gas by means of liquid air, followed by fractional distillation, by which process rather too little N_2O is found.

Hempel's third co-operator, Hering, studied the question (of equal importance for theory and for practice), whether in the vitriol chamber we have to deal with a simple process of oxidation, as again assumed by Wentzki (p. 1034 of our text), or whether, with the majority of chemists, we must assume the formation of an intermediate substance. Hering's experiments showed that N_2O_4 reacts much more slowly than N_2O_3, and that there can be no question of a simple oxidising process in the vitriol chambers, but that, according to the theories of Lunge, Raschig, and others, intermediate substances are formed. The temperature most favourable for the formation of sulphuric acid was found to be 70°. This formation goes on all the more easily the more water and the more nitrous gases are present and the better these gases are distributed. Even by a great excess of SO_2 and H_2O, and even at a higher temperature (73°), the nitric oxide is essentially only reduced down to N_2O, and but very small quantities of elementary nitrogen are formed.

Wentzki (*Z. angew. Chem.*, 1914, i. p. 112), in opposition to Hempel, still maintains that the formation of sulphuric acid in the chambers takes place without the formation of intermediate

CHAPTER VIII

THE PURIFICATION OF SULPHURIC ACID

Page 1045. *Injurious Effect of Arsenic in Sulphuric Acid.*—As mentioned in the text, ammonium sulphate made from gas liquor by means of strongly arsenical sulphuric acid turns yellow, owing to the formation of sulphide of arsenic. Parrish (*J. Gas Lighting*, 1916, cxxxiv. p. 134; abstr. *J. Soc. Chem. Ind.*, 1916, p. 535) mentions three methods for overcoming this difficulty: (1) Working with a film of oil or of anthracene on the surface of the acid in the saturator, which film retains both tarry substances and sulphide of arsenic. This method is used by shale distillers in Scotland. (2) Using a closed saturator with an automatic scumming device; the arsenic sulphide is discharged continuously with the tarry matter, without the use of an oil film. (3) Precipitating the arsenic from the acid by means of the waste gases from the saturator, containing H_2S. An apparatus for doing this in a continuous way is described in the original.

Page 1051. *Removal of the Arsenic.*—The Gräflich von Landsberg-Velen und Gemensche Chemische Fabrik A. G. (Ger. Ps. 252273 and 256234; Fr. P. 432874; Austr. P. 60964) produces sulphuric acid free from arsenic and iron by passing the burner-gases through a dry filter and then immediately through a denitrating column; in case of need the gases are

Eng., 1914, p. 334) is a horizontal washer, similar to those used in gas-works, consisting of several iron rings, enamelled inside by a special enamel, in which revolves an enamelled shaft, provided with agitating-blades, forty to sixty times per minute, which dip into the acid down to one quarter. The sulphuric acid flows in the opposite direction to the stream of H_2S, by means of overflows through the single compartments, and issues through a filter. The excess of H_2S is absorbed by caustic soda or milk of lime. These washers purify from 200 to 300 tons of acid per week, leaving only 1 to 1½ parts of arsenic in 1,000,000 parts of acid; the plant covers a ground space of only 7 × 5 ft. The apparatus is supplied by Davis Brothers, 66 Deansgate, Manchester, and has been introduced at many English factories.

Lihme (U.S. P. 1103522) purifies the gases intended for the manufacture of sulphuric acid, especially by contact processes, from arsenic by passing them through ferric oxide at 70° to 80° (*vide infrà*, p. 279).

Bithell and Beck (B. P. 1500, 1913) run the sulphuric acid through a tower, divided by horizontal diaphragms into several chambers. H_2S is blown into the bottom chamber and rises upwards from chamber to chamber by serpentine pipes.

Page 1069. *The removal of nitrogen oxides* from sulphuric acid, according to Grégoire (*Bull. Soc. Chim. Belg.*, 1914, p. 32; *Chem. Zentr.*, 1914, i. p. 1243), is effected by diluting the acid in a Kjeldahl flask with its own volume of distilled water, and strongly boiling up to its concentration. If after this treatment traces of nitrous compounds still remain in the acid, the treatment is to be repeated (and will even then hardly attain its purpose!).

CHAPTER IX

THE CONCENTRATION OF SULPHURIC ACID

Page 1087. *Lead Pans heated by Top Fire.*—Bernutat (Ger. P. 281133) passes the acid to be concentrated through a number of compartments, connected with one another, through which hot gases are conveyed in counter-current.

Page 1103. *Concentration by Steam-heat.*—The Norsk Hydro-Elektrisk Kvaelstofaktieselskabet (Fr. P. 459092) runs the acid through a tower heated by steam, and removes the water from the acid in three stages by employing steam of three, four, and five atmospheres' pressure. Steam of 3 atm. produces acid of 65 to 74 per cent.; steam of 4 atm., acid of 74 to 80 per cent.; and steam of 5 atm., acid of 80 to 85 per cent.

According to the Swiss P. 64234 of the same firm, dilute sulphuric acid is concentrated by distillation, treating the vapours with a drying agent in a drip-apparatus. A cooling agent is employed at least in one point between the still and the outlet of the vapours, in such a way that the temperature in the drying zone does not exceed the boiling-point of the dilute acid.

Pritchard and the United Alkali Company (B. P. 29542, 1913) describe a tubular apparatus for concentrating sulphuric acid by means of steam, in which the joints between the protecting mantles for the tubes and the lining of the evaporating-vessel are not exposed to the steam circulating in the tubes, and where the joints of the tubes with the vessel are not in contact with the acid.

patents of Bottomley and Paget by The Thermal Syndicate, Ltd., at Wallsend-on-Tyne.

According to the *Forty-fourth Report of the Alkali Inspector*, p. 28, the replacing of porcelain dishes by vitreosil dishes has had very favourable results, viz., reduction of the breakage of dishes, and therefore smaller losses of acid and fewer stoppages for replacing broken dishes.

According to *Chem. Trade J.*, li. p. 650 (of 21st December 1912), The Thermal Syndicate, Ltd., had supplied a government arsenal with 700 vitreosil dishes for concentrating sulphuric acid.

The paper of Bodenstein and Krauendieck (not Kranendieck, as the name is spelt in the text), on the velocity of the decomposition of sulphuric acid in contact with quartz-glass, has been mentioned in the text, p. 1561.

Voelcker & Co. (Ger. P. 258351) manufacture objects of quartz-glass with coloured or completely fused surfaces by fusing quartz sand round an electric resistance core, and uniting the quartz body by blowing; the latter body has previously received the desired quality of surface or colour by suitable treatment.

W. Hof. (B. P. 21291, 1913; Ger. P. 279131; U.S. P. 1099368) distils acids continuously by running them down in slightly inclined tubes of quartz-glass. Most of the acid is evaporated in the tubes; the non-evaporated liquid, together with the solid impurities, runs off at the bottom. The vapours of the pure acid are condensed. Up to a ton of sulphuric acid can be evaporated in twenty-four hours per superficial metre of the tubes.

The Aussiger Verein für chemische und metallurgische Fabrikation (Austr. P. appl. 4345) manufactures tubes of quartz by means of an electric flame-arc, produced in the hollow of the tubes to be made. This hollow is shaped before producing the electric arc, and is kept up by the same.

12 inches wide, and 4 inches deep.

Stoffmehl (Fr. P. 460627) concentrates sulphuric acid in a set of quartz dishes, placed partly inside and partly outside of a tower made of acid-proof material, in such manner that they are consecutively heated by the fire-gases. The dishes placed inside the tower are fed with the acid previously concentrated in the dishes outside the tower.

Zanner (B. P. 19841, 1914; Ger. P. 260655; Fr. P. 462016) effects the first concentration of sulphuric acid in two rows of quartz dishes, placed behind a muffle-furnace in a somewhat higher position. The first concentration is effected in the muffle-furnace, in similar dishes made of quartz or cast iron.

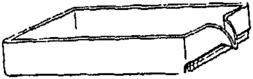


FIG. 19.

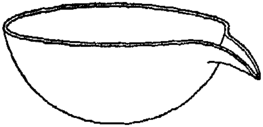


FIG. 20.

The cast-iron dishes may be placed in the bottom of the muffle, in such a way that their bottoms are directly heated by the flame.

Mason (*Met. and Chem. Eng.*, 1915, p. 17) describes an apparatus, composed of lead pans and quartz dishes, in which daily 4 tons sulphuric acid of 95·25 per cent. H_2SO_4 are made at a cost of 4s. 4½d. per ton; the exit-gases take only 2·23 per cent. of the acid away. *Cf.* also A. E. Marshall (*ibid.*, p. 136; *J. Soc. Chem. Ind.*, 1915, p. 350).

Pages 1123 and 1574. *Siloxide.*—As mentioned in the text, this name has been given to a substance obtained by combining with quartz a small proportion of zirconium and titanium. According to experiments described by Pohl (*Z. angew. Chem.*, Page 1123. *Silicon nitride* is recommended as material for constructing acid-concentrators by Herre (*Chem. Zeit.*, 1915, p. 348).

Tubes made of silicon are made by the Carborundum Company at Niagara Falls for conducting hot mineral acids.

Page 1127. *Cascade Apparatus for the Concentration of Sulphuric Acid.*—Mackenzie (B. P. 2389, 1913) constructs such apparatus of dishes, provided with a tubular continuation, in which there is a loose tube, capable of being turned. They may be made of glass, porcelain, lead, quartz, or "tantiron."

Green (B. P. 27209, 1911) employs rectangular pans, heated by hot gases, produced in a single fireplace, through which the acid is carried in parallel streams; further on single troughs through which the acid flows in two or more streams.

J. Harris (B. P. 7728, 1912) describes a cascade apparatus for the concentration of sulphuric acid.

Cascade apparatus for this purpose are also composed of "Field-tubes," as shown in Fig. 21, such as they have been employed for a long time in connection with steam-boilers; they have a particularly large heating surface, and are in this case made of quartz-glass, or "tantiron" (p. 1129); at their upper enlargement and at the bottom they are supported by moulded "gibsonite" blocks. The *Chem. Trade J.*, vol. li. p. 459 (1912), shows a cascade formed from such tubes.

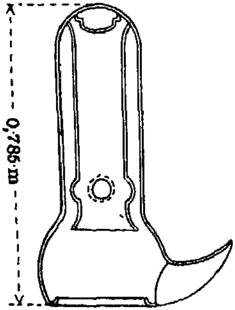


FIG. 21.

Carmichael and Guillaume (B. P. 15678, 1913) avoid the drawback observed in cascade apparatus, that the denser liquid has the tendency of remaining at the bottom of the vessels, by the next lower vessel. A special form of these vessels is described in B. P. 25802, 1913, of Beck, Bithell, and J. A. Beck & Son.

According to the Alkali Inspectors' Report for 1914, the cascade system for the concentration of sulphuric acid had been more and more extending. It is important to take care of a proper relation between the draught in the fire-flue and that in the flue carrying away the acid vapours. In several cases an improper escape of acid vapours was caused by the fact that the draught in the fire-flue was stronger than in the other flue, so that acid vapours went into the chimney instead of going into the condensing apparatus. The concentrating vessels are made of silica, tantiron (p. 1129), and in a limited number of cases of "ironac" (*vide infrà*).

The following remarks on the cascade system of concentration are made in the Inspectors' Report for 1915 (*Chem. Trade J.*, 1916, vol. lix. p. 303).

For the efficient and satisfactory operation of the cascade system it is essential that (1) a greater draught should be given to the flue leading the evaporated gases and vapours towards the condensers than is given to the fire-flue leading the fire-gases to the chimney; (2) excessive local intense heating of any section of the cascade be avoided; and (3) adequate means for condensing the acid vapours be avoided. Sufficient draught on the fume flue ensures the proper removal of vapours of evaporation; it thus increases the amount of work done by the plant, and at the same time prevents the objectionable acid fumes being drawn into the fire-flue, to pass thence by way of the chimney into the air. Intense local heating leads to badly balanced evaporation, to dissociation of the acid, with a consequent undue formation of fume, to violent ebullition in some of the vessels leading to breakages, entailing further

Basins of Silica, Ironac, Narki, and Tantiron, with Preheaters.

cid feed, strength °Tw.	Number of Basins.	Output Tons Acid per 24 hours (166-169 °Tw.).	Water and Acid evaporated per 24 hours. Tons per 100 basins. Loss of strong acid assumed to be—			Packing in condensers.			
						Per basin.		Per ton of strong acid made.	
			nil.	5 per cent.	15 per cent.	Volume, cubic feet.	Sectional area, square feet.	Volume, cubic feet.	Sectional area, square feet.
						Coke packing.			
105°	727	61·5 (=1·69 cwt. per basin.)	4·5	5·1	6·4	6·5	1·6	77	18
123°	1440	112 (=1·55 cwt. per basin.)	3·1	3·6	4·7	8·2	0·7	105	10
136°	40	4 (=2·0 cwt. per basin.)	2·7	3·3	4·6	6·2	1·2	62	12
147°	100	15 (=3·0 cwt. per basin.)	2·9	3·8	5·5	7·5	...	50	...
						Ring packing.			
120°	40	2·5 (=1·25 cwt. per basin.)	2·5	2·9	...	5·0	...	76	...

Cascade Plant and Condensers with Preheaters.

Acid feed, strength °Tw.	Description of plant.	Output of acid.		Packing in condensers.				
					Per basin.		Per ton of strong acid made.	
		Tons per 24 hours.	Strength, °Tw.	Nature.	Volume, cubic feet.	Sectional area, square feet.	Volume, cubic feet.	Sectional area, square feet.
110°	3 tantiron pans and basins .	5	168°	coke	...	...	43	7

31·1035 grammes):

Year.	Officially reported.	Altogether estimated.	Year.	Officially reported.	Altogether estimated.
1900	163,060	212,500	1907	172,752	310,000
1901	203,057	315,200	1908	156,792	250,000
1902	197,024	300,000	1909	164,118	264,000
1903	192,976	226,000	1910	175,716	275,000
1904	161,950	290,120	1911	180,400	300,000
1905	167,950	200,450	1912	177,375	300,000
1906	185,792	210,318			

According to *Z. angew. Chem.*, 1914, p. 100, the production of platinum in the Ural district in the year 1913 was 299 pood, 18 pounds; in the last eleven years altogether 3609 pood, 32 pounds; in 1914, 298 pood; in 1915, 215 pood.

According to *Chem. Zeit.*, 1914, p. 810, new important beds of platinum ore have been discovered in the west of the Ural district, the technical exploitation of which is to be energetically taken in hand.

Other considerable beds of platinum ore exist in the United States, especially in California and Oregon, and some in Canada. According to *United States Geological Survey*, the production of pure platinum from American ores in troy ounces has been:

Year.		Year.		Year.	
1903	110	1908	750	1912	1005
1904	200	1909	638	1913	483
1905	318	1910	773	1914	570
1906	1439	1911	940	1915	742
1907	357				

A new occurrence of platinum has been discovered in the Yellow Pine district in Clark County, South Nevada fine-grained quartz rock, lying in a system of longitudinal fissures, something like an irregular silica deposit in the Carbon-dolomite. For the purpose of inquiring into this occurrence, from 1000 to 2000 tons of ore were examined, which contained on an average per ton: 3·46 ounces of gold, 6·4 silver, 0·70 platinum, 3·38 palladium. These precious metals occur especially in a lead-iron sulphate, which has been called plumbojarossite; in some nests of this mineral 100 ounces of palladium and platinum are found, also gold here and there on a large scale. This discovery is very important, both from scientific and practical reasons. Certainly some primary occurrences of platinum metals are known in the Ural and in Colombia, but in all of them the platinum occurs only in traces, without any economical value. As a matter of fact all platinum is obtained from secondary occurrences. Hence the new Boss vein is the only primary occurrence possessing economical value, in which the platinum metals have the greatest importance among the precious metals. The only exception to this rule seems to be the sperrylite, discovered in the first years of this century in the copper ores of New Rambler, Wyoming. Of course the principal question is now: whether there is enough ore in the new district, and whether the amount of precious metals does not diminish in lower depths.

In California and Wyoming rocks have been discovered which contain platinum in such quantities that it would pay to recover it (*Chem. Zeit.*, 1915, pp. 523 and 552).

A new occurrence of platinum is in the Ronda Mountains, in Andalusia, in olivine rock, containing from 2 to 3 g. platinum per cubic metre (*Chem. Zeit.*, 1915, p. 892).

According to *Chem. Zeit.*, 1913, p. 760, Australia produces 300 to 400 oz. of platinum, Birma (*ibid.*, p. 1514) about 57 oz. According to *Chem. Zeit.*, 1913, p. 1452, in Germany (in the Westerwald) quite recently a bed of rocks has been several cases where platinum had been stated to occur in samples of rock this has been an error, caused by the presence of platinum in the reagents employed, especially in the oxide of lead.

The total production of platinum is stated in *The United States Geological Survey*, in troy ounces per annum :—

	1910.	1911.	1912.	1913.	1914.	1915.
Russia	275,000	300,000	300,000	250,000	241,200	124,000
Canada	30	30	30	50	30	100
Australia	332	470	778	1,275	1,248	56
Colombia	10,000	12,000	12,000	15,000	17,500	19,000
United States, from home crude platinum . .	390	628	721	483	570	742
United States, from home and foreign "matte and bullion"	1,000	1,200	1,300	?	?	?
Borneo, Sumatra, etc. .	209	...	200	...	...	...
Altogether . .	286,961	314,328	315,029	267,008	260,548	143,898

The yearly *consumption* of platinum is stated by Siebert (*Chem. Zeit. Rep.*, 1914, p. 84) at about 6000 kg., of which one-third is taken up by the chemical and electrical industries.

The *prices* of platinum from 1869 to 1912 are stated in the text, p. 1153. According to a decree of the Russian Government, dated 7th January 1914, crude platinum has to pay an export duty of 30 per cent. of its value (which is to be fixed by the Russian Council of Ministers), which is, of course, of immense importance for the business of the world.

In the year 1915 the price of platinum rose up to 7900 frs. per kilogram.

p. 7, the escape of acids in the average of all districts has been—

In 1911 . . .	0·708 g. per cubic foot.
1912 . . .	0·696 ” ”
1913 . . .	0·777 ” ”

Page 1148. *Faure and Kessler's System of concentrating Sulphuric Acid.*—For heating Faure-Kessler stills (as well as Gaillard's, etc.) the patent gas-producer of Zahn is recommended.

Page 1151. *Volatilisation of Platinum.* The United States Bureau of Standards (quoted in *Chem. Trade J.*, 1916, li. p. 139) states that there is no appreciable loss of weight up to 900°, but above this temperature the loss increases rapidly, most in the case of platinum containing iridium, and least in case of platinum alloyed with rhodium.

Page 1174. Kestner's new British patent for his apparatus, mentioned in the text, is No. 21548, of 1911.

Page 1179. Brandenburg (Ger. P. 243544) concentrates sulphuric acid in cylinders made of cast iron, quartz, etc., which at the bottom are continued into a cone with a lateral continuation, closed on the outside, which is heated, whereby a strong circulation takes place.

Harris (B. P. 7728, 1912) concentrates acid in horizontal pipes, passing at different heights through a heating flue and its walls in such a way that they can be singly removed and replaced without interfering with the others. The pipes connecting the ends of the horizontal pipes are shaped in such a way that the acid does not fill them entirely.

Brünler (Ger. P. 283790) evaporates sulphuric acid to about 62° Bé. in a continuous way in lead-coated or stoneware vessels introduced at the lower part of the chamber and directed by means of a baffle on to the surface of the acid. The concentrated acid collects at the bottom of the chamber, and the moisture-laden gases leave at the top.

Oliver, assignor to the Chemical Construction Co., Charlotte, N.C. (U.S. P. 1195075), passes hot gases over the surface of the acid, and then afterwards through a tower, jets of air being passed through the acid.

The Galizische Karpathen Petroleum A. G. vorm. Bergheim, Garvey, and Gellen (Ger. P. 271625; Aust. P. 60565) concentrate sulphuric acid in a cast-iron apparatus, shown in Fig. 22, consisting of a pan, *a*, provided with an outlet, *i*, for the concentrated acid, and heated by a direct fire, a lid, *b*, and an alembic, *c*. The latter, as well as the lid, *b*, is heated from the outside by the fire-gases in order to protect the distilling vapours from condensation. Pipe *d* carries away the vapours; its lower part is also surrounded by fire-gases. Within the alembic, *c*, there is a set of dishes, *f*, the lowest of which rests by means of the parts *g* on projections *h*, attached to the sides of pan *a*. The cover *b* may also be shaped in such

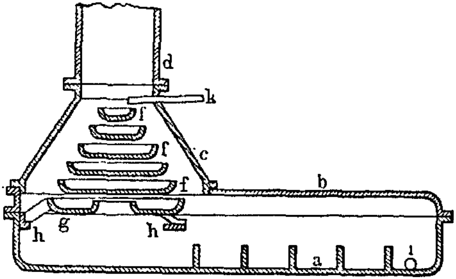


FIG. 22.

k on to the top dish. All the acid vapours escape through *d* either into a cooler or into a tower made of acid-proof material, fed by cold acid, which is thereby heated and increased by the condensing distillate.

Leitch (B. Ps. 1495 and 16001 of 1915) concentrates sulphuric acid continuously in three stages, first in lead pans up to 75 to 80 per cent., then in intermediate vessels of silica, glass, porcelain, tantiron, duriron, or ironac, arranged on the cascade principle, and finally to 96 to 98 per cent. The acid vapours are collected by hoods and condensed in a tower. The same inventor, in B. P. 16001, 1915, claims (1) maintaining the temperature of the acid as it passes to the first stage of concentration at from 100° to 125°; as it passes from the first to the second stage at from 135° to 150°; from the second to the third stage at from 200° to 215°; and during the third stage at from a minimum of 260° at the inlet to a maximum of 325° at the outlet. (2) A tower for heating the dilute acid, arranged at a level above the concentrating apparatus, above the final concentrating pan, and a duct for leading the hot vapours from the final concentrating pan to the tower. (3) A duct for leading the dilute acid from the storage reservoirs to the top of the heating-tower, and a duct leading the preliminarly heated acid to the first pan of the concentrating cascade. (4) A condenser arranged at a level above that of the concentrating plant, a duct for the gases between the top of the tower and the condenser, and other ducts for the hot vapours formed in the chamber to the condenser. (5) The chambers of the second and third stages of concentration are enclosed by means of easily removable covers to facilitate the cleaning of the plant and the making of repairs.

The Soc. an. la Fabrique de Soie Artificielle de Tubize (B. P. 10386 of 1915; Fr. P. 479320; Swed. P. 41077) concen-

Lennox (B. P. 23919 of 1914) employs a rotating drum with circumferential corrugations, dipping into a trough mounted on sliding rods, which is divided into compartments for every corrugation; the whole is enclosed in a casing. The compartments communicate with one another at alternate ends of the partitions. Hot air or the like is passed through the drum, and the acid drops on to the drum at the end remote from the hot-air inlet, and at a point in advance of the axial plane; the concentrated acid is withdrawn from the last compartment of the trough at the hot-air inlet end.

Recovery of Sulphuric Acid from Acid-Tar, Sludge-Acids, and similar Waste Products.

Page 1186. Lemaitre (*Chem. Zeit. Rep.*, 1913, p. 478) treats waste acids from the manufacture of dynamite by steam, superheated to 300° to 400°, or by hot air in connection with dilute sulphuric acid at 200°. The acid, after denitration, still contains from 2½ to 3 per cent. nitroso-sulphuric acid; this, on the concentration of the acid to 92 to 94 per cent. H_2SO_4, goes down to 0·15 per cent.

The Salpetersäure-Industrie Gesellschaft, Gelsenkirchen, employ their process for concentrating nitric acid (mentioned in the text, p. 195), also for treating the waste acids from nitrating operations; especially according to their B. P. 18113 of 1912.

Gellen (U.S. P. 1062025) runs the waste acid from refining oils continuously into a decomposing-vessel, placed in an outer vessel heated by a steam coil. The decomposing liquid is also run into the inner vessel; the mixture formed there runs over into the outer vessel, and from this into a settling-chamber, provided with a heating-coil, from which the recovered acid and the hydrocarbon oils run off continuously at different heights.

Bräunlich (B. P. 2695 of 1913; Ger. P. 267873) runs the by anorganic salts without evaporation with equivalent quantities of calcium carbonate and sand, made into a paste, with addition of a little water in an autoclave to 600° to 800°; pure sulphuric acid or sulphur trioxide distil off, and calcium silicate remains behind.

Kroupa (Austr. P. 67116) regenerates acid from acid-tar by running this in a finely divided state over heated fire-proof and acid-proof materials, with admixture of air.

Coster van Voorhut (B. P. 12363 of 1915; Ger. P. 292728) places waste acid from petroleum factories, after dilution with water to about 52° Bé., in a lead-lined, steam-jacketed autoclave, and forces in carbon dioxide until the pressure reaches 7 atm. Steam is then passed through the jacket until the pressure within the autoclave has risen to 10 atm. The heating is maintained for two hours, when the acid will have separated from the tar without any formation of SO_2 or SO_3. The acid and tar are then blown out of the autoclave separately. The CO_2 is washed and used over again.

Bühler (Ger. P. 287555) exposes the waste acid to hot gases, free from oxygen, at a temperature of 273° and upwards, by means of a rotating drum dipping into it. The coke residue left on the drum is removed by a scraper and also recovered.

Still (Ger. P. 291775) treats the waste acid in the hot state, in which it is sufficiently thin, with high-pressure steam or with a blasting-jet, produced by heated high-pressure gas. The sludge-acid thus treated at once separates into pure sulphuric acid and a granular residue, whilst the volatile substances escape together with the steam or gas.

Gasser (Ger. P. 272130) purifies the waste acid from the manufacture of benzol by forcing through it finely divided hot air. For this purpose the air previously employed for cooling obstruct the condensing-pipes, by passing the gases and vapours over a surface of water or dilute nitric acid, whereby the organic substances are solidified and deposit at the bottom of the water-vessel, whilst the water is gradually saturated with nitric acid.

The Phoenix A. G., Gelsenkirchen (Ger. Ps. 289162 and 289524), mix the waste acid from the benzol manufacture with ammonia water and with benzol wash-oil, tar-oil, or coal-tar, in order to obtain a concentrated solution of ammonium sulphate and an acid-free tar product by one operation. Or they add ammonia water, containing some chloride, to the mixture of waste acid and tar-oil, and pass steam through the mixture. Owing to the reactions which occur, the temperature rises considerably and the benzene and its homologues and hydrochloric acid are distilled off and collected.

Other patents for this object are:—Zdaska (Ger. P. appl. Z., No. 8310); P. and F. M. Murphy (U.S. P. 1094861); Kützer (B. P. 27977 of 1913); Blowski (U.S. P. 1186373)

Recovery of Sulphuric Acid from the Waste Acid produced in the Etching of Metals.

Howl and Perry (B. P. 5830 of 1914) recover the acid by evaporation until the whole of the dissolved iron has separated in the form of ferric sulphate.

T. A. Anderson (B. P. 3505 of 1914) mixes the waste acid with an excess of milk of lime, agitates for two or three hours, allows the precipitate (consisting of ferrous hydrate, calcium sulphate, and a little calcium hydrate) to settle down, and pumps it on to filter-presses. The cakes remaining in these are exposed to the air for a few days, until the ferrous hydrate has completely changed into ferric hydrate, which is used for the purification of gas or for the preparation of gypsum, according to whether ferric hydroxide or calcium sulphate prevail

Ferrosilicium has recently become a very important material for producing acid-proof vessels of all kinds, especially also for heating, distilling, etc. According to J. Hoffmann (*Chem. Ind.*, 1911, p. 241), the ferrosilicium prepared by Jouvé, and sold by the name of *Metillür*, resists the attack of all acids except fluohydric acid, and is also specially applicable for constructing concentrating vessels for sulphuric acid. Hermann (*Chem. Zeit.*, 1913, p. 750) certainly contends that ferrosilicium, in spite of its great resistance to acid, has not been extensively employed in chemical works because it has not been found possible to make large apparatus from this substance. But this is a mistake.

By the name of *Tantiron*, the Lennox Foundry Company, Ltd., at Glenville Grove, New Cross, London, S.E., sends out apparatus made of ferrosilicium, containing about 15 per cent. silicon, for the concentration of all acids, such as sulphuric, nitric, phosphoric, formic, acetic, butyric, etc. According to a communication of that firm, dated 30th June 1914, the Norsk Hydro-Elektrisk Kvaelstofaktieselskab has constructed its nitric acid plant entirely of tantiron, and enlarges it continuously, so that it requires from 200 to 300 tons of that material per annum. The same material is also employed by the Nitrogen Products Company (which works the Ostwald process, *v.* our text, p. 256), the Badische Anilin- und Sodafabrik, Nobel's Explosives Company, and most other manufacturers of blasting materials. In tantiron the crystalline structure of ferrosilicium is modified in such way that on cooling it behaves like ordinary cast-iron, and therefore admits of manufacturing from it apparatus of any size required. Once brought into this state, it may be remelted over and over again, without reverting to the crystalline structure of the alloys otherwise similar to it. It may also be turned, take also the following statements on apparatus made of tantiron. The price of these apparatus is certainly four times as high as that of ordinary cast-iron apparatus, but their duration is a thousand times that of the latter. There exist other metals and alloys resisting acids, but they cannot be employed for the manufacture of apparatus, as they cannot be cast and shaped by machinery. Tantiron is a hard, close-grained, silvery-white alloy, melting at about 1200°, not rusting, not oxidising, and not sensibly attached by the ordinary corrosive substances. Castings varying from a few ounces up to many tons in weight can be made of it with equal facility. The following table shows the loss of weight by the action of the substances treated in this book on tantiron:—

Loss of Weight of Tantiron, per cent.

	First 24 hours.	Second 24 hours.	Third 24 hours.
Nitric acid, specific gravity 1·4 . .	0·03	0·01	...
" " 1·1 . .	0·01	...	...
Sulphuric acid, 98 per cent. . .	0·10	0·02	0·02
" 30 " . .	0·07	...	...
Fused sulphur	0·06	0·01	...

One hundred g. tantiron lost on boiling for seventeen hours:—

In	Sulphuric acid of 10 per cent. . .	0·13 g.
"	Nitric acid of 25 per cent. . . .	0·10 "
"	Hydrochloric acid of 30 per cent. . .	0·16 "

Its conductivity for heat is almost the same as that of iron; its hardness = 35 (that of iron is = 24, copper = 8, regulus metal = 2·2, platinum = 6, lead = 1, quartz = 52, stoneware = 32); its specific gravity = 6·9. It conducts heat twice as much as lead, and four or five times as much as quartz or stoneware.

It is an alloy rich in silicon, low in carbon, and produces most excellent castings, as the metal when molten runs as fluid as water. During the last few years Haughton's ironac has had a very wide application in sulphuric acid and nitric acid plant. It successfully withstands the action of boiling sulphuric or nitric acid, either dilute or concentrated; samples which have been in contact even with boiling acids of low densities for upwards of twelve months display no appreciable loss, and do not appear to have thrown down any traces of free iron in solution. Ironac is in fact a most extraordinary alloy, and behaves entirely differently to many so-called acid-resisting metals, which have been abandoned as being unsuitable for industrial purposes. Among the widest applications of ironac is that for concentrating sulphuric acid and nitric acid, and rectifying plant for these acids. Ironac is very largely used for preheating trays and cascade basins in open-type concentration or Benker plant (p. 1121), coolers, beakers and beaker-pipes, Webb's beakers (p. 1124), leading in and out pipes for Kessler plant (pp. 1141 and 1191), calottes and support apparatus for this plant; for pipes, pumps, flue-covers, and all other parts of acid-concentrating plant. Orders are on hand for Great Britain and Ireland, Russia, Spain, Italy, Switzerland, the British Colonies, and America. Owing to its absolute resistance to nitric acid of varying densities, it is largely in demand for the government explosive factories and dynamite works, both in England and on the Continent. Cooling-columns and pipes for the condensation of nitric acid, denitrating towers, etc., are now being regularly made of ironac. The ironac pumps for nitric acid have proved more satisfactory than any other pumps for that material, being much stronger than stoneware and more effective. In the industries of aniline, celluloid, and other large users of nitric acid, ironac has been worked, from *nickel*, *cobalt*, *tungsten*, *molybdenum* and the metals of the *platinum* group.

Grimshaw (*Chem. Eng.*, xvii., No. 2; *Chem. News*, 1913, p. 283) prepares very strongly acid-resisting alloys, by first alloying 40 parts *cobalt* with 60 parts *tin*, and dissolving a sufficient quantity of this in *copper* to obtain alloys of 80 to 95 parts copper with 20 to 5 parts $Co+Sn$. These alloys resist nitric acid to such an extent that it would take from five to seven years to dissolve a layer 1 mm. thick.

Strzoda (B. P. 26732, 1913; Ger. P. 272158) employs for pipes serving for the concentration of acids, in the place of platinum, porcelain, etc., ordinary cast-iron pipes, coated inside with *neutral iron* (*cf.* p. 1188), which is absolutely acid-proof; the unavoidable intermediate space between that coating and the cast iron is filled with an acid-proof cement, made of baryta, asbestos, kieselguhr, and sodium silicate solution. The inventor explains his process in *Z. angew. Chem.*, 1914, i. p. 455, and points out that thereby pure limpid sulphuric acid of 98 to 99 per cent. H_2SO_4 can be obtained without any wear and tear of the apparatus; a result not obtainable by any other material, not even platinum.

Zeno (Ger. Ps. 248857 and 273292) obtains acid-proof vessels by means of a coating of *aluminium*, which is first treated with a solution of caustic alkali, and then, without washing this off, with a solution containing cupric chloride or sulphate, potassium-iron tartrate, ferric chloride, zinc chloride, and tin chloride. The metallic coating thereby formed is washed to remove the adhering solution, heated, and provided with an acid-resisting layer of carbon by immersion in a mixture of oil and balm and subsequent ignition.

centration to 66° Bé. (92 to 94 per cent. H_2SO_4). Sp. gr. of feeding-acid, 52·6° Bé.; consumption of coke, 1400 kg.; quantity of acid of 65·6° Bé. (=92·15 per cent. H_2SO_4) produced in twenty-four hours, 15290 kg. The apparatus can produce acid up to 98 per cent. H_2SO_4. The Alkali Inspectors' Report for 1914 states that the Kessler system was being successfully worked and more and more extending. The Report for 1915 considers it one of the best existing; but its extension is limited by the lack of a suitable material for the vessels.

Page 1200. The United States patent for the apparatus of Vialleix and Perrin, mentioned in the text, is No. 1066557; the Austrian patent, No. 54965.

Pohl (in the paper quoted in the text) states the following advantages of vitreosil (quartz-glass, *vide* pp. 1123, 1129, 1147, and *suprà*, pp. 247 *et seq.*) over the volvic lava employed by Kessler. The latter is inclined to become tender, especially in plants worked intermittently, whilst vitreosil is not in the least damaged. Vitreosil pipes have much thinner walls than lava pipes, but they are made with the same external dimensions, so that they can be put into existing plants without any alterations. The greatest difficulty in the working of Kessler plants is the frequent breakage of the porcelain bells, instead of which bells now made of vitreosil are employed, of the shape shown in Fig. 23, which fit to the lower parts in the existing apparatus. These are now provided with depressions into which fit the opposite parts of the bells, so that these are always placed exactly over the centre of the lower parts. In 1912 there were twelve Kessler plants, provided with vitreosil bells and lower parts, in daily use.

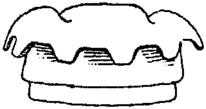


FIG. 23.

into the chimney. If the acid is to be very pure, the boxes are provided with thin covers, with holes protected by caps, for the escape of the aqueous vapour. The first concentration may, of course, also be effected by lead pans, in a spray-tower, etc. The main concentration takes place in the muffle, B, built of material proof against acid at high temperatures, such as firebricks, quartz, cast iron, etc. It is entirely closed, and heated outside by fire-gases. Within the muffle there are open boxes, *c c*, made of quartz, which receive the previously concentrated acid by the pipes *b*, and after concentration allow it to run out by the pipes *d*. The acid vapours formed here are conducted by pipe *e* to the cooling-worm or box. The number of quartz boxes in the muffle, B, must correspond to the demands made upon the performance of the apparatus. These boxes may be suspended, or placed on the bottom of the muffle, or both. In some cases, *e.g.*, when concentrating to 97 to 98 per cent. H_2SO_4, the last boxes (which are in this case preferably made of cast

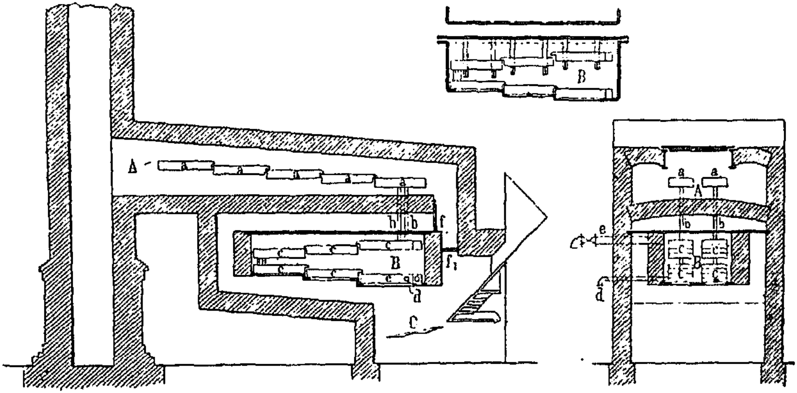


FIG. 24.

FIG. 25.

producers, by Zahn's high-pressure gas-producers, described in Ger. Ps. 190660 and 237238. This apparatus acts continuously, and can be worked with coal, coke, wood, or any other fuel. At the end of 1913 it was applied in seven Gaillard acid-concentrators, in one Kessler apparatus, one Hartmann and Benker apparatus, one lead-pan apparatus heated from below and four heated from the top, all of them working with coal, not with coke, and yet furnishing very pure acid.

According to the Alkali Inspectors' Forty-ninth Report (for 1912), p. 14, the Gaillard apparatus was satisfactorily working in many British factories; only in one factory they had difficulties with the exit-gases, which they hoped to overcome by applying more condensing apparatus. The Fiftieth Report (for 1913), p. 12, also speaks very favourably of this system. In the concentration of the chamber acid, the sulphates less soluble in concentrated acid separate as crusts at the bottom of the concentrating-apparatus. Such crusts formed in Gaillard towers consisted of $Fe_2(SO_4)_3,H_2SO_4$ and $Fe_2O_3,4SO_3$; the latter compound also occurs in the crusts forming in platinum stills.

Page 1208. Düron (*Chem. Zeit.*, 1914, p. 559) quotes the results of working his apparatus for producing concentrated sulphuric acid of various strengths, up to monohydrate or fuming acid. According to his B. P. 344 of 1913; Ger. Ps. 257559 and 257573; Fr. Ps. 453733 and 453742; Austr. P. 62173, the heating gases are conducted in parallel branches perpendicularly to the direction of the current of acid over the top of this, thus exposing the acid several times to the action of the hot gases. Two gas flues are arranged at the longitudinal sides of the concentrator, and are connected by transverse channels; they are connected in turns with the entrance and the exit flue. An acid channel runs in the longitudinal direc-

		Kg.	Per cent.	Horse-power.	£.
Düron	92 to 93	12,750	6·8	2 to 2½	1100 to 1250
	97 „ 98	6,100	13·5		
Gaillard	92 „ 93	12,500	8 to 9	1½ „ 2	2500 „ 2250
	97 „ 98	6,800	16·5		
Kessler	92 „ 93	10,700	9 to 10	11 „ 12	1500 „ 1750
	97 „ 98	4,000	20 „ 22		

Other apparatus for concentrating sulphuric acid by hot air:—Sohlmann and Wilson (U.S. P. 1009196); John Harris (B. P. 7728, 1912); Pfannenschmidt and Moss (B. P. 13642, 1914).

Concentration of Sulphuric Acid in a Vacuum.

Page 1210. Further patents of Krell (Ger. Ps. 166557, 176994; Fr. P. 363604; Austr. P. 21305).

The Norsk Hydro-Elektrisk Kvaelstof A. G. (Ger. P. appl. N15431) employs a series of vacuum apparatus on the tubular system. In the first apparatus the acid is brought up to 60 to 69 per cent., in the second to 75 per cent., in the third to 79 per cent. SO_3. The French patent is No. 474995.

Emptying Acid-carboys, etc.

Page 1220. Rabe (*Z. angew. Chem.*, 1911, p. 403) describes an arrangement for running corrosive liquids from store tanks into bottles or open vessels by means of taps. The outflowing jet is converted by radial ribs into parallel streams, and any lateral squirting is thereby avoided. In order to avoid any retention of liquid, the ribs are made to slant towards the centre at the place where the liquid enters.

Other contrivances for running off acids have been described (*suprà*, p. 131) in connection with nitric acid.

Page 1224. *Vessels for storing and carrying Sulphuric Acid.*

and must be regularly controlled and repaired.

E. G. Hoyt, as reported in *The Brass World*, June 1913, has patented a lead-compound coating particularly adapted for the above-mentioned purposes, consisting of a thick upper layer of soft commercial lead, and a thin lower layer of an alloy of 80 to 98 per cent. lead with 20 to 2 per cent. antimony, which is welded on to the soft lead; on rolling out a plate is formed, the surface of which is soft and the bottom hard; this composition keeps its form better than ordinary soft lead.

Ernst (*Chem. Apparatur*, 1916, p. 93; *Z. angew. Chem.*, 1916, ii. p. 370) describes in detail the coating of iron vessels with lead, copper, aluminium, nickel, etc.; also with india-rubber, paints, etc.

On vessels for keeping acids made of aluminium, cf. *suprà*, p. 66.

According to *Eng. and Min. World* of 28th March 1914, cement vessels, coated with Trinidad asphalt-mastic, have been found suitable for storing sulphuric acid. After twelve months they showed no change, while all other materials tried failed.

Jordan (Ger. P. 280863) coats vessels for the transportation of acids, made of glass, stoneware, etc., with three layers, united by fusion, the innermost consisting of a mixture of bituminous and fibrous substances (jute, hair, etc.); the central one is an elastic mixture of wool, peat, etc., and the outside layer bitumen, strengthened by sand or gravel.

In *Chem. Ind.*, 1915, p. 214, a case is mentioned where a steamer, loaded with 2800 tons of sulphuric acid stored in iron drums, came to grief through leakage of the acid.

According to *Chem. Trade J.*, 1915, lvii. p. 152, in August 1915 a lawsuit was brought in the United States by The Reid-Donald Steam Company against C. Tennant, Sons & Co., claiming damages to the amount of £70,000 for the loss of

H. N. Morris (B. P. 8370 of 1916).

Expense caused by the Use of Platinum for the Concentration of Sulphuric Acid.

Page 1252. In the cost of producing concentrated sulphuric acid, the amortisation of the platinum apparatus is a considerable item. The price of platinum having greatly increased since the statements of cost were got up for the last edition, the cost price of acid made by apparatus in which platinum is employed has correspondingly gone up. But we abstain from going into figures about this, since between the date of publishing this book and that at which it is consulted by the reader, further great changes in the price of platinum may take place, in an upward or in a downward direction.

Page 1255. *Niederführ and Lüty's Calculations.*—The figures given in the text were misprinted, as will be readily observed by the reader. They should read:

Minimum. Marks.	Maximum. Marks.
1·037	...
...	1·191
1·207	1·207
2·244	2·398

CHAPTER XI

THE MANUFACTURE OF NORDHAUSEN OR FUMING OIL OF VITRIOL AND OF SULPHURIC ANHYDRIDE

Various Processes for Manufacturing Sulphur Trioxide or Fuming Oil of Vitriol, otherwise than by Contact Action.

Natho (Ger. P. 265835) heats a mixture of equivalent quantities of calcium sulphate and silica with a little water in an autoclave. According to his assertion, the conversion of the mixture into calcium silicate and SO_3 is complete at 600° to 800°, at which temperature the SO_3 is not yet decomposed.

Page 1274. Briggs and Merriman (this name is erroneously spelt "Merriam" in the text), in their U.S. P. 1082301, transferred to the General Chemical Company, give further details on their process, protected by their U.S. P. 1013638. They describe an apparatus for producing fuming oil of vitriol, consisting of a tower, fed on the top by sulphuric acid divided into small streams, whilst the gases containing SO_3 enter near the bottom. The tower has an outlet for the air, and is provided with contrivances for cooling its contents, to the extent of about 1 superficial in. of cooling-surface to every 3 cub. in. of active tower space.

The U.S. P. 1047576 of W. Schultze and the General Chemical Company, for preparing a double anhydride of gas separates out in the form of sulphuric acid of 3 or 4 per cent.; by shocks against solid surfaces more acid is separated, showing a sp. gr. of 40° Bé.

The Manufacture of Sulphuric Anhydride, Fuming Oil of Vitriol, and Ordinary Sulphuric Acid by Contact Processes.

Page 1275. The name "Winckler" in the footnote to this page should be changed into "Winteler."

Page 1326. A lecture by Dr Caspari, reported in the *Chem. Trade J.*, 1914, liv., p. 336, in which the *theories of the contact process* are treated, contains no new matter.

Page 1326. *Statistics* on the Manufacture of Sulphuric Anhydride, etc., by Contact Processes.

According to the Alkali Inspector's Report for 1913 (L., p. 5), there were in the United Kingdom during that year ninety sulphuric acid factories of Class II. at work, but how many of these were working with contact processes (which are included in that class) is not stated.

In Germany, in 1912, eight factories were working entirely on the contact system, and fifteen factories employed this together with lead chambers.

In Sweden (*Z. angew. Chem.*, 1915, iii. p. 721) so much fuming oil of vitriol is now made that the formerly important importation of that article has entirely ceased.

In Holland (*Chem. Zeit.*, 1913) there is a factory working on that system.

Page 1342. *Contact Process of the Badische Anilin- und Sodafabrik.*—Their B. Ps. 23541 of 1913 and 8462 of 1914 (taken out by J. Y. Johnson on their behalf) prescribe passing desired shape, heated at 300° to expel the ammonia, and then at 440° in gases containing sulphur dioxide, to produce cohesion; or a mixture of 316 parts of kieselguhr with an aqueous solution of 50 parts of ammonium vanadate and 56 parts of caustic potash is evaporated nearly to dryness, and the residue formed into granules and heated at 480°, first in gases containing sulphur dioxide and afterwards in air. Instead of pumice, sodium-ammonium silicate ("permutite") may be employed as carrier.

Their Ger. P. 291792 states that vanadic acid or its salts, if mixed with finely divided indifferent porous substances, has catalytic properties, equal or nearly equal to those of platinum.

Their Ger. P. 292242 enumerates as catalysers alkaline salts of osmic and ruthenic acid, and as carriers of these salts also asbestos, magnesia, alumina, pumice, and meerschaum.

Page 1348. The Badische's Fr. P. 414387 for destroying the contact poisons contained in the gases is mentioned on p. 1421.

Their B. P. 12977 of 1913 (taken out by J. Y. Johnson) prescribes soaking asbestos, meerschaum, etc., in a solution of alkali osmate or ruthenate; and drying. The contact mass thus obtained can be employed either directly, or after being heated, or acted upon with acid or reducing agents.

Their B. P. 1358 of 1915 (Norw. P. 26822) describes the preparation of catalytic agents by impregnating zeolite or sodium-aluminium silicate with solutions of potassium-platinum chloride, or osmate, or ruthenate, or tungsten chlorides.

Page 1358. *Contact Processes of The Tentelew Chemical Company.*—Further patents:—

For the purification of pyrites-burner gases:—B. Ps. 3327 of 1891 and 15948 of 1898; U.S. Ps. 900500, 937147, and 937148.

In the year 1914, according to *Chem. Zeit.*, 1914, p. 811, Page 1375. *Manufacture of Sulphuric Anhydride, Fuming Oil of Vitriol, and Sulphuric Acid by Contact Processes in the United States.*—A new patent of the General Chemical Company is U.S. P. 1082301.

We now give some more details from the communication of Patterson and Cheney (*J. Ind. Eng. Chem.*, 1912, p. 723; *Chem. Trade J.*, 1912, li. p. 293), briefly mentioned in the text, p. 1575, on contact sulphuric acid from brimstone, by the process of Schroeder and Grillo (p. 1382).

The plant described by the authors was erected in 1907 at the U.S. Naval Proving Ground, Indian Head, Md., for the manufacture of acid used in making smokeless powder. With a rated capacity of 6 tons, it was operated successfully for three years, burning pyrites. During the last two years Louisiana brimstone has been used entirely, with a view to increasing the capacity without enlarging the plant, and evidently it was hoped to reduce costs, notwithstanding the large increase in price per unit of sulphur. The expectations in both respects have been fully realised.

The burner used is a Tromblee and Paull burner (*vide suprà*, p. 157); it consists of a horizontal cylindrical shell, 8 feet long and 3 feet in diameter, with conical ends, revolving once in two minutes. At one end is a hopper and worm feed with sliding dampers. The other end is connected with a rectangular cast-iron box of 37 cubic feet capacity, provided with a sliding damper and a vertical cast-iron uptake pipe, which leads to a brick dust-catcher. The burner is rated at 5500 lb. per day, but easily gets through 6000 lb. When forced along by the worm, the sulphur melts just before it drops into the body of the burner, forming a complete liquid coating on the inside of the revolving shell. Any sulphur volatilised from the cylinder is completely burned in the combustion box and uptake. At the end of the dust-catcher the gas has cooled to a temperature of air lift for circulating a stream of sulphuric acid from the pot to the scrubber, which is divided horizontally by perforated diaphragms. The air lift was designed by one of the authors, Patterson; it works with only 5 lb. of air pressure, raising 80 lb. of acid per minute; the top of the lift is gas-tight; the air being piped to the gas system, there is no loss of SO_2 at this point. From the scrubbers the gas passes to a second lead-lined coke box exactly like the first, and thence to a pair of dry filters in parallel, which complete the purification; the gas is then carried into the main building. Throughout the purification the gas comes into contact with no other metal than lead, but beyond this point either cast iron or wrought iron is used entirely.

Within the house the gas first passes through a positive pressure blower, by regulating the speed of which the composition of the entrance gas is controlled, and the movement of the gas through the whole system is completed. Manometers on either side of this blower show a suction of 1·5 in., and a pressure of 0·75 in. of mercury. Just forward of the blower is the sampling pipe, where the composition of the gas is tested by the usual iodine solution.

The next step is the conversion system, which includes a preheater and converter. The preheater consists of a series of vertical iron U-pipes and headers, placed in a furnace heated by soft coal to 380°, this temperature being required for proper catalytic action of the contact mass. The converter, placed close to the preheater, is a vertical cast-iron cylinder, 6 ft. in diameter and 8½ ft. high, composed of five horizontal sections. Each section contains a wire-mesh tray for supporting the contact mass, and a baffle to properly spread the gas. The contact mass is anhydrous magnesium sulphate, containing 0·2 per cent. of finely divided platinum. A total quantity of 5900 lb. of coarsely granulated mass is spread on the trays to a depth of vertical cast-iron cylinder, 15½ ft. high, resting on a cast-iron base, the top being covered by a perforated plate, from the centre of which rises the exit-pipe for waste gases. It is lined with acid-proof tiles, and packed with quartz rock. The gas enters on one side near the bottom. A constant stream of acid is pumped on to the top plate, percolates through the quartz packing, and passes out at the bottom of the tower to a cooling-pipe. This is a horizontal, water-cooled U-pipe, one leg of which carries an overflow pipe connected with a pump and the collector. The acid supplied to the top of the tower is kept at a temperature of 79°, and has a strength of 99·5 per cent. H_2SO_4; the strength of the acid leaving the bottom of the tower is reduced by the addition of a constant small stream of acid of 75 per cent. H_2SO_4, just before it enters the cooler.

The reservoir of this weak acid, the mixer, and the strong-acid tank are mounted on a platform in the centre of the building at a sufficient elevation for the acid to flow by gravity. The reservoir is an open lead-lined box, holding 1000 gall. The mixer is a lead pot, provided with lead coils for cooling-water, and a specially designed mixing-pipe in which water and strong acid are brought in contact. The mixing-pipe consists of two heavy ¾-in. lead pipes, set at an angle of 30°, and held together by a heavy lead sheath burned on to a short length of 1½ in. lead pipe. One of the ¾-in. pipes carries strong acid from the head tank, and the other ordinary cold water from the mains. The 1½-in. pipe serves to carry the mixture to the pot without spatter. This type has the advantage of minimum repair, and mixes about 5000 lb. of 75 per cent. acid per hour. The head tank has a capacity of 18,000 lb. of strong acid. The product of the plant passes through the scale tank, and is delivered to the nitric-acid plant, where in winter weather it is mixed with 2 per cent. nitric acid, to prevent freezing. The entire product can be delivered at 99·5 per cent. H_2SO_4, but for counteracted by raising the temperature of the gases entering the converter, and for this reason hardly any two plants burning pyrites will be found using the same initial temperature. The catalytic properties of "poisoned" mass may be improved by sprinkling it with aqua regia, and expelling the arsenic by the heat of the converter, or they may be entirely restored by heating the mass in a furnace after sprinkling with aqua regia. Another factor in conversion is the quantity of SO_2 contained in the gas entering the converter. With pyrites it is customary to use an entrance gas containing not over 5·5 per cent. SO_2, with the mass in good condition. When "poisoning" has occurred, this percentage must be reduced to obtain good conversion.

In this plant, using Louisiana brimstone for eighteen months, no indications of "poisoning" have been apparent, and the converter has not been opened. The temperature of the gas entering the converter is kept constantly at 380°, and the conversions are regularly 95 to 95·5 per cent. This low temperature means a decided saving in coal and wear and tear on the preheater. During six months the average consumption of coal has been 21·8 lb. per 100 lb. of SO_3 made. An entrance gas of 6·5 to 7 per cent. SO_2 is regularly used. During six months under the above conditions, the average make has been a little more than 6 tons of acid per day, and the average yield on the sulphur fed to the burner 93·36 per cent. The plant can make a maximum quantity of 8 tons with a yield of 90 per cent. Comparisons of cost sheets show that by changing the raw material from pyrites to brimstone, the cost of manufacture has been reduced nearly two dollars per ton of 98 per cent. acid; this result is due in part to minimising losses from shut-downs for repairs, in part to increased yields, and in part to saving in coal and cost of upkeep.

washing, etc., for the removal of the substances preventing the subsequent sursaturation, and then produces in them, by means of thermodynamic changes of state of the auxiliary constituent, or by introducing several auxiliary substances in succession, a sursaturation increased up to the formation of fog. This fog is separated from the gases by electric treatment, or centrifugalling, or in other ways. The sursaturation is produced by repeated gradual addition of steam and sulphur trioxide. The gas to be purified may be carried *gradatim* first through a sursaturating place for the gaseous fog-producers, and then to a precipitating place for the fog when formed in an ascending even stream.

Herreshoff and the General Chemical Company, New York (U.S. Ps. 940945 and 1113437) remove the moisture from the pyrites- and pyrrhotite-burner gases intended for the manufacture of sulphuric acid by the contact process, by interposing in the gas-conduit a cooling arrangement in the place where the gases, after being treated in a scrubber with sulphuric acid of 40° Bé., have a temperature of 90° to 95°. The cooling apparatus is so constructed that it reduces the temperature of the gases to about 38°. The condensing liquid is always immediately removed.

The Metallbank und Metallurgische Gesellschaft, Frankfurt a.M. (Fr. P. 456524), filter the gases through a material, obtained by gradually heating cotton or the like in closed vessels to 300° to 350°.

Lihme (U.S. P. 1103522, assigned to the Grasselli Chemical Company, Cleveland) filters the pyrites-burner gases, and then brings them into contact at temperatures from 70° to 90° (anyhow not above 100°) with metallic oxides capable of absorbing arseniuretted hydrogen, such as iron oxides. After once more filtering, and in case of need drying the gases, a shape accessible in all parts, and provide them with a preliminary heater of tubular spirals.

Grosvenor (U.S. Ps. 1036609 and 1036610) moves the contact mass forward in countercurrent to the stream of gases; the contact chamber is a cylinder, transformed by partitions into a spiral channel.

The Farbenfabriken vorm. Fr. Bayer & Co. (B. P. 1994, 1912; Ger. P. 263287; Fr. P. 453470) describe an apparatus for the catalytic treatment of gas mixtures, which is already mentioned *suprà*, p. 96. So is the apparatus of Wilhelmi (*ibid.*).

R. Heinz provides the contact carriers with raised and lowered parts, in order to increase their active surface and to retard the velocity of the gases by the friction.

Theodore Wolff (U.S. P. 1099530) describes an apparatus for the *gradatim* treatment of gases in contact apparatus, consisting of a considerable number of contact and heat-exchanging compartments placed successively over one another, and directly connected with each other; also an arrangement by which a gas mixture is passed into the first contact compartment, and an arrangement by which a desired quantity of this gas mixture is passed through the heat-exchanging compartment before entering into the first contact compartment.

C. *Various Contact Substances.*

A. de Montlaur (Ger. P. 267868) describes contact bodies for chemical catalyses, consisting of mica in the form of leaves, ribbons, or plates, provided with a chemically produced covering of precious metals, as platinum, gold, silver, in a brilliant and firmly adhering form. For this purpose the compounds of these metals with thiosulphate are employed, such as are employed in porcelain painting; from these the

E. Taylor and F. P. Bergh (U.S. P. 1157455) project finely divided iron oxide as a cloud into a mixture of sulphur dioxide and air, and control the temperature of the reaction by injecting a stream of cold air, or other cooling medium, into the gases. The iron oxide is collected, either by settling or by an electric dust-collector, and is used again in the process.

G. Schicht A. G. (Austr. P. 70771) saturate kieselguhr or similar porous masses with nickel carbonyl, and heat the mass to effect the precipitation of metallic nickel. The nickeliferous powder so obtained is immediately worked up to a paste, with exclusion of air, with oil, or other suitable substance.

Page 1401, line 5. The B. P. of the Verein Chemischer Fabriken, Mannheim, is No. 17266 of 1898 (misprinted 17255).

Page 1432. *Regeneration of Spent Contact Masses.*—Kelsey, Depew, and the New Jersey Zinc Co. (U.S. P. 1047236) regenerate platinum contact masses which have become inactive by allowing a mixture of nitric-acid and hydrochloric-acid vapours to act upon the mass at 425° to 550°.

Page 1436. C. Böhm (*Chem. Ind.*, 1913, p. 120) recommends ignited cerite earths as catalysers. The sulphates of the cerite earths, after being heated to 700° to 1000°, furnish good catalysers for the manufacture of SO_3. The presence of praseodymium peroxide, etc., has a favourable influence.

Conidelon, Soc. an., Antwerp (B. P. 5174, 1913; Ger. P. 266190), add to a solution of vanadic acid or other vanadium compounds salts of iron, and a reagent precipitating iron and vanadium compounds. Since, in the manufacture of sulphur trioxide, superheating sometimes occurs up to 800°, the vanadium contents of the contact mass must be kept low enough to avoid even at such temperature the formation of easily fusing compounds, which by reducing the active surface of the contact mass obstruct the passage of the gases. The precipitation may ammonium chloride formed.

The vanadium catalyser of the Badische is mentioned *suprà*, pp. 273 *et seq.*; also their catalysers prepared with osmium and ruthenium compounds.

Silver and vanadium are employed as catalysers for the manufacture of SO_3 by the Farbenfabriken vorm. F. Bayer & Co. (B. P. 15165, 1913; Ger. P. 280960; Fr. P. 460014). *E.g.*, asbestos is impregnated with ammonium metavanadate, then treated with argentic nitrate, and washed. When employing asbestos containing 20 per cent. argentic vanadate at a temperature of 520°, the SO_2 of pyrites-burner gases is almost quantitatively transformed into SO_3.

Kéler and Weindel have obtained the U.S. P. 1102670 for the employment of argentic vanadate as catalytic substance.

Classen (Ger. P. 274345) employs as catalysers for the manufacture of SO_3 metallic chromium, or alloys of iron with chromium, vanadium, molybdenum, silicon and manganese, silicon, aluminium, and manganese, or mixtures of these alloys. They are not sensitive to contact poisons, and in that respect they are far superior to platinum, and much more active than manganese, uranium,. tungsten (wolfram). Molybdenum-iron is best prepared containing 50 to 60 per cent. molybdenum; it allows of converting SO_2 into SO_3 at 400° to 550°.

C. Ellis, The Ellis-Foster Co., and Parsons (U.S. P. 1103017) state that selenium and tellurium have the advantage over platinum as catalysers for the formation of SO_3 that the gases require no purification except removal of the flue-dust. The temperature must be always kept below the fusing-point of the contact mass. The best mass is that which contains from 5 to 15 per cent. selenium of the weight of tellurium; it is dissolved in dilute nitric acid, and employed by impregnating asbestos, etc., drying and cautiously heating. The oxidising action is promoted by working at a pressure of 1 to 2 atm. Their U.S. Pa earths, Mg, Al, Zn, etc., containing from 1 to 4 per cent., or at most 5 per cent. tungsten, preferably 1·4 per cent. They are prepared by squirting out the paste and heating.

Sabatier and Mailhe (B. P. 2011, of 1915) employ a network of wires, blades, rods, or tubes of catalytic materials, heated to the necessary temperature by an electric current. Suitable catalytic materials are metals of the platinum or nickel series, or their alloys, or tantalum. The metallic network may be embedded in finely powdered metals, metallic oxides or carbonates, etc., of Th, Zr, U. Ti.

Dewar and Liebmann (B. P. 12981, 1913) reduce by means of hydrogen at comparatively low temperatures a mixture of hydrated or anhydrous oxides or carbonates of two or more catalytically acting metals: nickel, cobalt, copper, and iron, or a mixture of the oxides of these metals with finely divided palladium, platinum, or silver. Or else a mixture of the above-mentioned oxides with silver is employed. They find it most favourable to employ for the preparation of the anhydrous oxides a mixture of nitrates, obtained by evaporating an aqueous solution. Preferably asbestos or other porous substances are employed as carriers of these catalysers. The following example shows how this invention can be carried out. Dissolve 98·2 parts of nickel nitrate (with 6 mols. water of crystallisation) and 9·3 parts cupric nitrate (with 6 mols. water of crystallisation) in water, heat the solution, add caustic soda in slight excess, bring the mixture to boil, collect the precipitate formed on a filter, remove the soluble salts by washing with hot water, and dry the washed precipitate first on a water-bath, and then in a drying-oven at about 130°. The reduction of the oxygen compounds thus obtained by means of hydrogen is almost perfect after two hours' treating at about 70°.

Sulzberger employs as catalyser nickel silicate, treated with hydrogen, whereby nickel and silicon are formed in the free prepared according to H. J. Hannover's B. P. 25702 of 1911. These are obtained by heating alloys a little over the melting-point of the more easily melting metals, and removing the fused portion by gas pressure, suction, centrifugal action, impact, or agitation.

Achenbach (Ger. P. 278402) employs a mixture of metallic silicon and boron.

Spencer, Kellogg, & Sons (U.S. P. 1111502) prepare a catalyser by treating dry aluminium oxide with a solution of palladium.

Wells (U.S. P. 1179484) coats fragments of glass with about 1 per cent. of their weight of reduced nickel.

Bassett (U.S. P. 1197381) employs a mixture of ferric hydrate and gypsum.

D. *Absorbing Apparatus.*

Page 1438. According to Schiffner (*Chem. Zeit. Rep.*, 1914, p. 383) the process of Cottrell, mentioned in the text, is working successfully in a number of American factories. Experiments made with it in Freiberg also yielded good results.

The absorbing tower of Briggs, Merriman, and the General Chemical Company, mentioned in the text, p. 1274, and *suprà*, p. 272, is also intended for treating the gases of contact apparatus.

Nagel (*Chem. Zeit.*, 1914, p. 514) absorbs the SO_3 by sulphuric acid, with the aid of a spraying apparatus, set into motion by the sulphuric acid.

Testing of the Gases produced in the Manufacture of Sulphur Trioxide by Contact Processes.

Bodenstein and Pohl (*Z. Electrochem.*, 1905, xi. p. 378) pass the gases into a measured quantity of iodine solution, retitrate the excess of iodine by sodium thiosulphate, and thus find the quantity of SO_2 present. By titrating the decolorised

The percentage yield of SO_3 is :

$$\frac{(b-2a)\times 100}{b-a}.$$

The process of Rabe (*Chem. Zeit.*, 1901, p. 345) has been briefly mentioned in the text, p. 1417. We here describe it more fully. Samples both of the burner-gases and of the gases produced in the catalytical apparatus are passed through 10 c.c. of decinormal iodine solution. If the number of c.c. of gases required for decolorising the solution before catalysis is called a, that required after catalysis is called b, the degree of conversion is indicated by the formula :

$$x = \frac{(b-a)100}{b-a}.$$

If the contents of the gases are stated in per cent., a denoting the percentage of SO_2 before conversion, and b the percentage after passing through the contact apparatus, the formula is :

$$x = \frac{20{,}000(a-b)}{a(200-3b)}.$$

The apparatus of Henz described *suprà*, p. 236, in connection with the exit-gases from Gay-Lussac towers, may be equally well used for the exit-gases from catalysing operations.

The method of Ljungh mentioned in the text, p. 1439, is altogether misleading. It consists in passing a sample of the gases slowly through a measured quantity of seminormal soda solution and retitrating the unsaturated soda by acid and methyl-orange; then adding two drops of acid, diluting and running the liquid into centinormal iodine solution, after addition of starch solution, up to decolorisation. From these titrations Ljungh calculates the relation of $SO_2 : SO_3$. This method is quite wrong; for during the absorption of SO_2 in soda employed by Rabe, as just described, is free from this objection.

Page 1441. *Combination of the Contact Process with the Lead-chamber Process.*—Such a combination is described by Wilke, and is mentioned in our text, p. 1576, where that name is erroneously given as "Wilde." His paper is printed *in extenso* in *Chem. Trade J.*, 1912, li. p. 294.

Page 1441. *Carriage of Fuming Oil of Vitriol by Water.*—The rulings made by the United States Steamboat Inspection Service in June 1915 (as quoted in *Chem. Trade J.*, 1915, lvii. p. 104) for the transportation of chemicals on steam-vessels carrying passengers contain the following prescriptions referring to "Oleum":—

"Oleum may be accepted and transported when packed separately in glass bottles of not more than 5 lb. or 5 pints' capacity, well cushioned, and separate from all other chemicals, or in small iron drums. Carboys or similar receptacles are unsafe. This commodity in 1-lb. bottles, but not more than five bottles in one lot, may be shipped in the same case with other chemicals, except the chlorates and chemicals of similar nature, if surrounded by a sufficient amount of satisfactory absorbent, such as mineral wool, sifted ashes, or infusorial earth. The packages in all cases should be labelled 'Acid,' and must be transported on deck."

CHAPTER XII

OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID

Page 1444. The Norske Aktieselskab for Elektrisk-kemisk Industri (Norw. P. 24038) obtains ammonium sulphate by the action of gases, containing SO_2 and NH_3, in the presence of steam, after transforming the SO_2 partially into SO_3 in well-known manner.

Page 1447. Burkhardt (B. P. 29568 of 1912) allows gases containing SO_2 to take up in a "unidirectional" electric current the whole of the aqueous vapour required for the reaction before they come into contact with nitrous sulphuric acid.

Sulphuric Acid from Gypsum.—Natho (Ger. P. 265835) makes a paste of gypsum and sand with a little water, and heats it in an autoclave for several hours to 600° to 800°, by which process the splitting up of SO_3 into SO_2 and O is to be avoided.

Cantilena (Ital. P. 413166; *Abstr. Amer. Chem. Soc.*, 1914, p. 1331) mixes finely powdered burnt gypsum and dried clay in such proportions that the ratio $(SiO_2+Al_2O_3+Fe_2O_3)$ CaO ranges between 0·43 and 0·50. The mixture is made up with water into a paste which can be moulded into bricks 20×10×0 cm. Only so much of the mixture is taken that the working into bricks does not require more than from five to ten minutes. After setting, the bricks are heated in furnaces in which the coal cannot come in contact with the mass heated, and in which there is always an abundant current of air and a temperature of to the sulphuric acid apparatus.

The Elektrizitätswerk Lonza (Swiss P. 72627) makes sulphuric acid from gypsum and quartz in an atmosphere much richer in oxygen than air, whereby any dissociation of SO_3 into SO_2 and O is prevented.

The Badische Anilin- und Sodafabrik (Ger. P. appl. B 79367) converts gypsum by means of magnesium carbonate into magnesium sulphate, and obtains from this the oxides of sulphur by heating with or without admixture of carbon.

Page 1449. *Manufacture of Sulphuric Acid from Sulphates.* —*Cupric Sulphate.* Perry (B. P. 20063 of 1911) treats a solution of cupric sulphate with hydrogen sulphide, whereby by the reaction:

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

sulphuric acid is set free. The precipitate of CuS is reconverted into $CuSO_4$ by the sulphuric acid obtained. [This process, as a matter of fact, does not furnish sulphuric acid, but merely converts dilute H_2S into concentrated H_2S!]

Ferrous Sulphate.—Weeks (U.S. P. 1048247) blows a solution of ferrous sulphate in the shape of spray into the upper end of a slightly inclined revolving-furnace which is from below heated by a gas-fire or otherwise, to such an extent that the decomposition of the sulphate is complete, but the SO_3 is not yet dissociated, but can be recovered in a tower by absorption in water or dilute sulphuric acid.

Page 1453. *Manufacture of Sulphuric Acid by calcining Pyrites with Salt.*—A mechanical furnace for this purpose is described in the B. P. 16450 of 1912, of Sutcliffe.

From Coal-gas.—Numbers of patents have been taken for converting the sulphur compounds, contained in a coal-gas, into SO_2, and utilising this for the production of ammonium sulphate, but as no free commercial sulphuric acid is produced by these

Leitch (B. P. 15455 of 1915) continuously extracts by means of a solvent nitro-compounds from waste acids from nitrations by running together in suitable proportions the solvent and the acid into a mixing vessel, containing stirring apparatus, and allowing the mixture to flow into settling tanks through an overflow pipe.

CHAPTER XIII

BY-PRODUCTS OF THE MANUFACTURE OF SULPHURIC ACID

Cinders from Non-cupreous Pyrites.

Manufacture of Ferrous Sulphate.—At the factory of Schnorf Brothers at Uetikon, near Zurich, the pyrites cinders are put into hot Glover-tower acid, with constant agitation. When the reaction is finished, the mass is dissolved in water, and reduced by iron shavings to ferrous sulphate. The liquor is now evaporated to 35° to 36° Bé. (measured at 90°), and allowed to cool, strips of iron being suspended in it. The ferrous sulphate obtained by crystallisation is cheaper than that made by dissolving iron in sulphuric acid, and there is no troublesome evolution of hydrogen.

Page 1456. *Use of Pyrites Cinders for the Production of Iron in Blast-furnaces.*—Polysius (Ger. P. 277854) agglomerates pyrites cinders by means of surface heating on a revolving dish or roller, until they are sintered, for use in a blast-furnace.

Schwarz and Lourié agglomerate the pyrites cinders for use in blast-furnaces by à mixture of Portland cement, granulated blast-furnace slag, and sulphate of soda.

The Metallbank und Metallurgische Gesellschaft, Frankfurt a.M. (Ger. Ps. 210742 and 241644), moisten the cinders with a solution of ferrous sulphate and with dilute sulphuric acid, mix the mass with fuel and allow it to solidify.

and the addition of steam to the compressed air, blown into the mass at the bottom, in such proportions that the top layers always remain damp, and that from the steam water-gas is formed, the combustion of which promotes the sintering of the mass.

The Internationale Wasserstoff A. G., Frankfurt (*cf.* their Ger. P. 220889 in the text, p. 1459), according to Ger. P. 244733 employ for reducing the ferric oxide in pyrites cinders water-gas, as rich as possible in hydrogen, instead of the otherwise used producer-gas, because from the latter, owing to the reaction: $2CO = CO_2 + C$, there is always some free carbon deposited upon the iron, and in the subsequent treatment of the latter by steam causes the production of impure hydrogen. The process is carried out in vertical, U-shaped iron tubes, heated by producer-gas to about 800°, and yields gas containing 98 per cent. hydrogen, at a cost price of 10 to 20 pfennig per cubic metre. This process is employed for military aeronautic purposes in Germany and France. The pyrites cinders have these advantages over the otherwise used micaceous iron ore: that they retain their hardness even after prolonged use, and that, owing to their great porosity, they offer a very large surface to the action of the steam.

Buddaeus (Ger. P. 273277) describes a process for sintering pyrites cinders, in which the fuel required for sintering is arranged in vertical columns, parallel with the current of air.

Page 1464. *Extraction of Zinc from Pyrites Cinders.*—Schmidt and Desgraz (Ger. Ps. 261307 and 261800) fuse the cinders with suitable fluxes, and filter the melted mass through metallic iron, whereby zinc, practically free from iron, is obtained.

Uebbing (*Metall und Erz*, x. p. 607; *Z. angew. Chem.*, the use of calcined alumina and spathic iron ore.

Buddaeus (Ger. P. 278064) adds to the liquors, after precipitating the copper by iron, a sufficient quantity of bases or carbonates to completely precipitate the ferrous and zinc oxide. The precipitate is dried with access of air, and from the product, consisting of ferric oxides, zinc oxide, and calcium sulphate, the zinc oxide is obtained by dissolving in acids.

Page 1470. *Selenium* is obtained by Klason and Mellquist (Swed. P. 35177; *vide suprà*, p. 204) by filtering the burner-gases before getting to the towers, through a tight filter of asbestos, etc., from which it is afterwards removed by heating or dissolving.

According to *United States Min. Resources* for 1911, i. p. 977, in the year 1910 10674 lb. of selenium was obtained as a by-product in the electrolytic refining of copper; in 1911, a larger quantity (not stated).

Extraction of Copper from Pyrites Cinders.

Page 1489. The Bayerische Aktiengesellschaft Heufeld (Ger. P. 254840) employ for the chlorinating and sulphatising roasting-process kilns provided at the bottom with a carrying-screw and a step-grate.

The same firm (Ger. P. 254253) describe arrangements for conveniently discharging the roasted material in continuous work, and other improvements in the roasting-kilns.

Page 1497. Ramén (Ger. P. 293541) describes an apparatus for treating roasted ores in order to facilitate their lixiviation.

Page 1500. The Mackay Copper Process Co. (Ger. P. 278153) treat the roasted material with a 2 per cent. solution of ferric chloride, which possesses a much superior acting property than concentrated solutions; nor does it require heating. The solution of FeCl is easily recovered; no basic salts are formed the silver in the metallic form. From the mother-liquor sodium sulphate can be obtained. Some further modifications are also proposed.

A method for quickly estimating the copper in pyrites cinders is described by Koelsch (*Chem. Zeit.*, 1913, p. 753). Ten g. of the cinders is heated with 6 to 7 g. sodium hypophosphite (NaH_2PO_2 aq.) and 40 c.c. hydrochloric acid (sp. gr. 1·16) diluted with 100 c.c. hot water, and precipitated with 50 c.c. of a sodium-sulphide solution, containing 40 g. $Na_2S,9H_2O$ per litre. The precipitate is agglomerated by agitation, filtered after five minutes, washed with hot water, and ignited in a porcelain crucible; a little sulphuric acid is added, and the excess of it removed by heating. The residue is washed into a beaker, and the copper is separated by electrolysis; or else, where it is not necessary to work with the utmost accuracy, the filter with the precipitate is heated with 10 c.c. nitric acid of sp. gr. 1·4, until no more ruddy vapours escape; the nitrous acid is destroyed by adding a little urea, the solution is made faintly ammoniacal, neutralised by acetic acid, potassium iodide is added, and the titration performed with thiosulphate in well-known manner.

Van Arsdale (U.S. Ps. 1119477 and 1119478) roasts copper ores, containing pyrites, with or without addition of sodium chloride, lixiviates the product, adds sulphur dioxide, and precipitates the copper by electrolysis. The electric treatment is stopped as soon as there is a precipitation of sulphite, and the remaining acid solution is applied for lixiviating a fresh quantity of ore.

Page 1514. *Precipitation of the Copper from Sulphate Liquors.*—The Metals Research Co., New York (Ger. P. 293967), lixiviate the substance in the presence of a little free sulphuric chlorinating roasting of pyrites cinders from lead and zinc, by passing the coke-oven gases into those liquors, so that these metals are precipitated as sulphides. In order to separate copper and zinc, the coke-oven gases are passed through the liquor up to the point where practically all the copper has been precipitated as CuS, a corresponding quantity of free acid being formed. After removing the CuS, the liquor is neutralised, *e.g.*, by calcium carbonate, and more coke-oven gas is passed in, whereby the zinc is precipitated as pure ZnS. The acid formed hereby must be always instantaneously saturated, in order to attain the complete separation of the zinc. If the liquor contains other metals, *e.g.*, lead, nickel, cobalt, etc., these are also precipitated and can be separated.

Weldon (B. P. 5607, 1882) proposed obtaining the copper from the liquor by the solution of calcium chloride, formed in his chlorine-regenerating process, which produces a mixed solution of copper and sodium, holding calcium sulphate in suspension. The latter is removed by filtration, and the copper precipitated by lime. This proposal has evidently found no practical application.

Spinzig and Wannag (Ger. P. 255454) electrolyse the liquor, employing the extracted solution at the same time for extracting the ore placed in the electrolyser, forcing the electrolyte mechanically through the annular space between the anode and a cathode cylindrically surrounding it, whereby injurious by-reactions on the precipitated metal are avoided. For the same purpose sulphur dioxide may be forced through the hollow anode against the outside cathode. A suitable apparatus is described.

Weeks (U.S. P. 1048247) obtains from the liquor sulphuric acid and ferric oxide by spraying it in a sufficiently highly heated revolving furnace, and absorbing the vapours in a cylinder by means of water or dilute sulphuric acid. The

the ferrous sulphate, and passed through a filter press.

Page 1529. *Statistics on Pyrites Cinders.*—Austria, in the year 1913, imported 118452 tons pyrites cinders for the recovery of iron, and exported 28293 tons.

Germany (*Chem. Ind.*, 1913, p. 493; 1914, p. 323) produced:

Year.	Pyrites cinders.	Blende cinders.
	Tons.	Tons.
1909	535.311	379,856
1910	602,639	386,242
1911	750,202	403,405
1912	809,485	470,347

In the South of France sulphuric acid is employed for the extermination of noxious weeds. The acid deprives them of water and decomposes the salts contained in the protoplasma. For some weeds acid of 8 to 10 per cent., for others acids of 12 to 14 per cent., is required. This treatment also applies to destroying snails, and is also efficient for combating some of the diseases of corn. For one hectare of soil 1000 litres of dilute acid are employed.

Statistics.—United Kingdom of Great Britain and Ireland.

The Alkali Inspector's Reports quote the following number of sulphuric-acid factories. (No. I. refers to lead-chamber works, No. II. to other factories, merely concentrating acids or working by contact processes):

	1907.		1908.		1909.		1910.		1911.		1912.		1913.	
	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.	I.	II.
In England and Ireland	154	89	152	86	151	88	150	90	149	89	146	89	146	90
In Scotland .	20	14	20	14	20	14	20	14	20	14	20	14	20	14

The number of sulphuric-acid factories has, therefore, slightly diminished during recent years, but their production has increased. It may be assumed that for a number of years past roundly a million tons of H_2SO_4 has been produced.

In 1911 there was imported 3076 tons ; exported 4764 tons sulphuric acid.
„ 1912 „ „ 0 „ „ 1040 „ „
„ 1913 „ „ ? „ „ 8525 „ „

	Tons.	Tons.
1912 1913	98,573 130,256	75,962 64,968

Year.	Production of acid, calculated as H_2SO_4.	Pyrites burnt.	Blende burnt.	Other Ores, Gas-oxides, Sulphur, Hydrogen Sulphide.
	Tons.	Tons.	Tons.	Tons.
1911	1,500,230	916,265	479,329	104,583
1912	1,649,981	981,556	554,750	79,892

Year.	Cinders obtained	
	From Pyrites, Lead and Copper Ores, Matte.	From Blende.
	Tons.	Tons.
1911	750,202	403,405
1912	809,785	470,347

Number of sulphuric-acid factories in Germany:

Year.	Total.	Lead-chamber works.	Contact works.	Works employing both processes.
1911	112	86	7	17
1912	109	83	8	15

In the year 1913 eighteen new sulphuric-acid factories were being erected for sulphuric acid, and one for anhydride.

Austria-Hungary:

Year.		Importation.	Exportation.
		Tons.	Tons.
1912	Ordinary sulphuric acid . .	36,501	16,066
	Fuming O.V.	213	150

300,000 tons, calculated as acid of 60° Bé. There were in that year in Belgium twenty-six factories working with lead chambers of about 400,000 cb.m. contents.

Sweden in 1911 produced in nine factories (one of which makes fuming acid) 126,810 tons sulphuric acid, calculated as 50° Bé.; in 1912, 126,749 tons.

Spain in 1911 produced 16,000 tons sulphuric acid from roasted ores.

Russia.—According to *Chem. Trade J.*, li. p. 353, the production of sulphuric acid (what strength?) in 1911 was nearly 230,000 tons, the importation 2735 tons. In 1912 the production was 256,000 tons. Eight factories worked with contact processes; four of these used the Tentelew process (p. 1357). A reporter in *Chem. Ind.*, 1914, p. 65, states the importation of chamber acid and concentrated acid into Russia in 1910 = 138,000 pood, in 1911 = 169,000 pood, in 1912 = 199,000 pood.

United States.—According to the *Mineral Resources of the United States for* 1912 (vol. ii., p. 949), and for 1914 (vol. ii., p. 148), and the report of Phalen in the *United States Geological Survey*, the production of sulphuric acid in the United States, expressed in short tons, has been:

	1911.	1912.	1918.	1914.
Acid of 50° Bé. . . .	1,026,896	1,047,483	1,643,318	1,628,492
„ 60° „	421,165	451,172	509,929	551,955
„ 66° „	751,541	774,772	797,104	916,192
Other strengths (exclusive of acids over 66° Bé.) .	10,728	66,166	63,158	65,890
Altogether .	2,210,300	2,339,593	3,013,509	3,162,439
The same calculated as acid of 50° Bé. . .	2,688,456	2,876,000	3,538,980	3,762,417 and 21993 tons

From copper-works .	207,057	321,156	336,019	348,727
„ zinc- „ .	230,643	292,917	296,218	411,911
Calculated as acid of 50° Bé. . . .	438,300	614,073	...	...
	547,875	764,237	790,296	950,911

In 1915 (*United States Geological Survey*, quoted in *Chem. Trade J.*, 1916, p. 507) the American production of sulphuric acid was: acid of 50° to 55° Bé., 1,518,271 short tons; acid of 60°, 657,076 tons; acid of 66°, 1,019,024 tons; other strengths, including fuming acid, 187,795; altogether, expressed in terms of 50° acid, 3,868,152 tons (of 2000 lb.). These figures include the acid produced at copper and zinc smelters, which amounted to 1,056,830 short tons, expressed in terms of 50° acid, and 59,189 short tons of oleum of different strengths.

According to *Chem. Trade J.*, 1913, p. 642, there were in 1909 in the United States forty-two factories in which the principal product was sulphuric acid, nitric acid, and mixed acids; besides further quantities of acids were made as by-product in many other factories, altogether in 183 factories. From 1904 to 1909 the consumption of brimstone for acid production increased by 8·3 per cent., that of pyrites by 87·6 per cent.; five factories worked the gases from roasting copper sulphide and blende. Of the total value of products, sulphuric acid represented 57 per cent., nitric acid 5·1 per cent., mixed acids 14·6 per cent. The total production of these acids increased 21·9 per cent. in value during the decade 1899-1909.

The exportation of sulphuric acid from the United States has been: 566 short tons in 1911; 10,248 tons in 1912; 6587 tons in 1914; 38,906 tons in 1915.

Argentina, according to *Chem. Zeit.*, 1913, p. 713, possesses only one sulphuric-acid works, which produces only 1500 tons acid per annum; the importation of sulphuric acid in 1911 produced 2197 tons.

India (*Chem. Zeit.*, 1914, p. 388) has two sulphuric-acid works which burn Sicilian, sometimes also Japanese brimstone, and which have already destroyed the competition of European importers.

Japan.—According to government returns, quoted in *Chem. Trade J.*, 1916, lix. p. 7, the production of sulphuric acid in Japan in the year 1915 amounted to 153,420,000 lb. (what strength?).

The World's Consumption of Sulphuric Acid in 1910 (what strength?) is estimated by Caspari (*Chem. Trade J.*, 1914, p. 234) in tons:—

	For superphosphates.	For other purposes.	Altogether.
Great Britain	350,000	650,000	1,000,000
Germany	530,000	850,000	1,380,000
United States	1,120,000	480,000	1,600,000
France	650,000	250,000	900,000
Italy	320,000	80,000	400,000
Austria	87,000	213,000	300,000
Belgium	155,000	95,000	250,000
Russia	35,000	115,000	150,000
Japan	(?)	(?)	80,000

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